

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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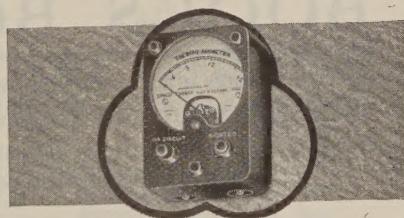
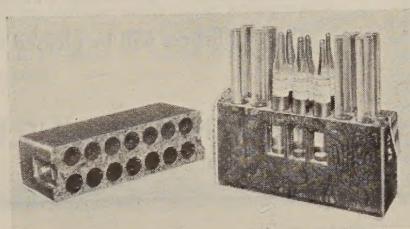
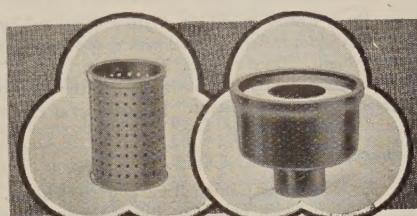
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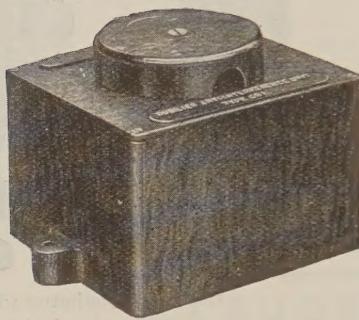


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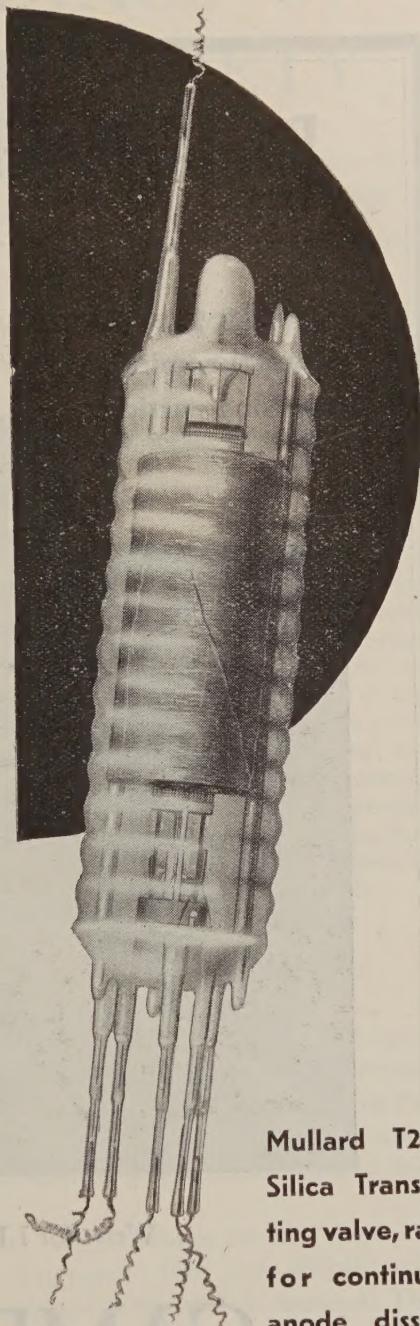
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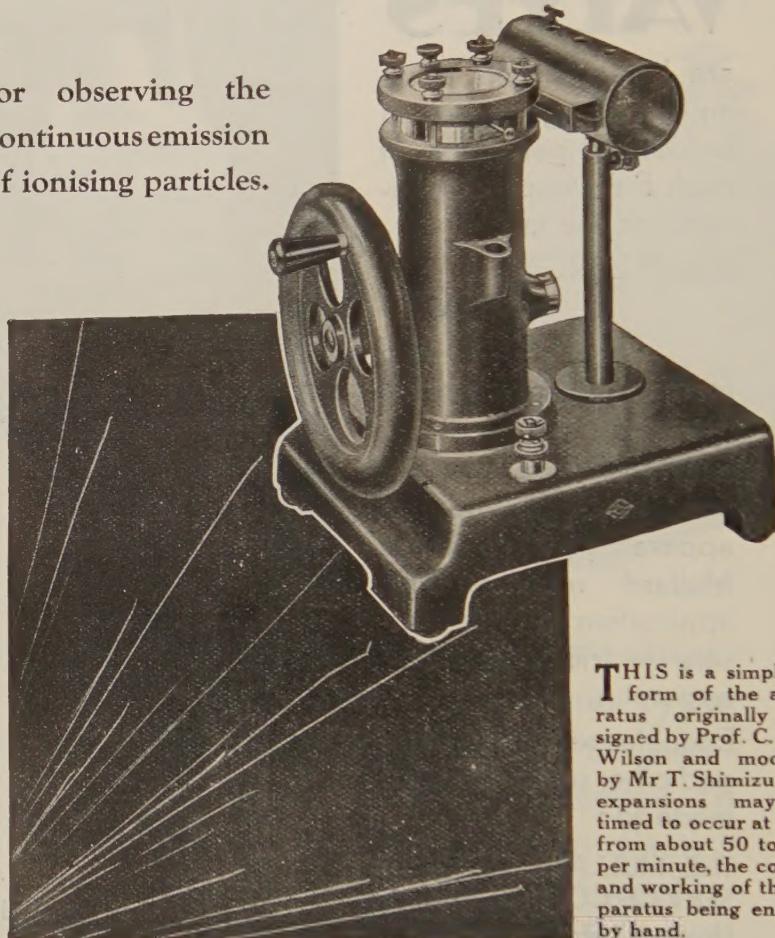
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THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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THE REFLECTING POWERS OF ROUGH SURFACES AT SOLAR WAVE-LENGTHS

By H. E. BECKETT, B.Sc., Building Research Station.

Received November 4, 1930. Read and discussed February 6, 1931.

ABSTRACT. A study of the reflecting properties of building materials for solar radiation has been made, a hemispherical mirror being used for integrating diffusely-reflected energy upon a thermopile receiver. The paper follows the work of Coblenz and Royds and deals at length with the errors inherent in the method and with the adjustment of the apparatus. The theory of the method is simplified by the introduction of an auxiliary specimen which, in particular, renders the observations independent of the degree of blackness of the thermopile receiver. Reflecting powers for a large number of building materials are given for four radiation bands within the solar range, and also for the composite radiation obtained by the screening of a pointolite lamp with a thin gold film. The latter radiation somewhat resembles that of the sun in range and distribution, and enables the reflecting power of a surface for total sunlight to be determined approximately in a single reading. The apparatus has been tested with magnesium carbonate surfaces and yields reflecting powers in the visible spectrum in good agreement with those found photometrically.

§ I. INTRODUCTION

In the course of an investigation of the heating effect of the sun's radiation upon buildings it was found that the reflecting characteristics of building materials had hitherto received little attention. As no apparatus capable of measuring the reflecting powers of rough surfaces over the solar wave-length range was available, it was decided that apparatus upon which such measurements could be made should be set up at the Building Research Station.

The methods previously used in examining rough surfaces are well discussed by Coblenz* and need not be detailed in this paper. That now adopted was developed concurrently by Royds† in Germany and Coblenz* in America. The incident radiation passes normally on to the specimen through a slot in a hemispherical mirror. The latter collects all radiation reflected from the specimen and

* W. W. Coblenz, *Bull. Bur. Stand.*, 9, 283 (1913).

† T. Royds, *Phil. Mag.*, 21, 167 (1911).

focusses it on the receiving surface of a thermopile. The necessary integration of reflected rays is thus performed by the apparatus, and the determination of reflecting powers becomes a routine operation when once certain errors inherent in the method have been evaluated. By the use of filters, radiation from various spectral regions may be allowed to fall on the specimen and the variation of its reflecting power with wave-length determined.

When an attempt was made to set up and use apparatus of this type, following very closely the specifications of Coblenz, numerous experimental difficulties were encountered. Although great accuracy was not essential in view of the variable nature of the materials to be examined, the opportunity has been taken to investigate certain errors which seem to have escaped previous notice. It is therefore with the adjustment of the apparatus and with the correction of the results that the present paper mainly deals.

§ 2. DETAILS OF THE APPARATUS

The general lay-out of the apparatus is shown in figure 1. The image of a slit S suitably illuminated from behind is projected by means of the concave mirror M_1 and the plane mirror M_2 on to the specimen, which is placed alongside the thermopile in the diametral plane of the hemispherical mirror M_3 .

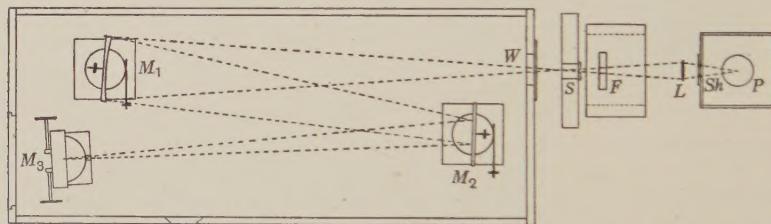


Fig. 1. Plan of apparatus.

The source and slit. The tungsten bead of a 100 c.p. pointolite lamp P provides a convenient source of high intrinsic brilliancy. The lamp operates normally with a current of 1.32 amp. and by substitution of an adjustable rheostat for part of the series resistance it is possible to maintain this current constant in spite of considerable fluctuations in the supply voltage. The necessary current check is provided by a high-grade ammeter whose scale is illuminated and viewed through a convex lens. In this way the current can be maintained constant to 0.002 amp. or about 0.15 per cent. The control-rheostat and ammeter are placed near the galvanometer scale and it is found that, with practice, observations can be made by a single observer. The lamp is mounted in an asbestos-cement screen which carries a brass shutter Sh operated through a string-and-pulley system.

As readings beyond the wave-length 3.0μ have not been required, a glass lens L of 10 cm. focal length is used to throw an image of the pointolite bead upon the slit. It may be shown by a simple analysis that the energy available in the apparatus is greatest for a given lens if the latter is placed at such a distance behind the slit

that the solid angles subtended at the slit by the lens and the concave mirror are equal. The source is placed so that its magnified image falls upon the slit. The lens used measures 5 cm. in diameter and is 50 cm. distant from the slit, thus allowing ample room for the insertion of a stand for filters.

The slit measures 5 mm. by 1 mm. and is mounted on a brass plate blackened on the side facing the concave mirror to prevent the reflection of stray light into the optical path. The image cast upon the thermopile measures 8 mm. by 1·6 mm.

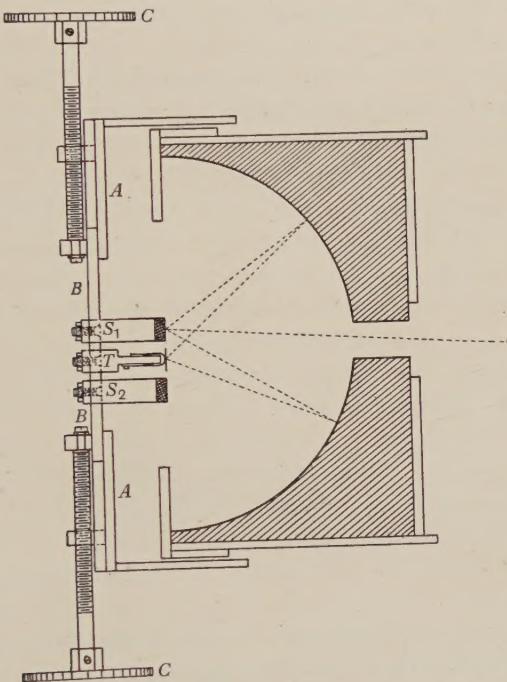


Fig. 2. The hemispherical mirror.

The mirror system. To prevent tarnishing, the three mirrors, which are surface-silvered, are mounted inside a wooden box whose atmosphere is dried with calcium chloride and kept free from sulphides with lead acetate. The dimensions of the curved mirrors are as specified by Coblenz: the concave mirror is 17 cm. in diameter and of 100 cm. focal length, and the hemispherical mirror 10 cm. in diameter with a slot 2 cm. by 1 cm. to admit the incident radiation. The hemispherical mirror is fixed in a cylindrical brass housing, figure 2, which is screwed to the base of the box. The other mirrors also are screwed to the box, but each has two rotational movements which enable accurate adjustment of the position of the reflected image to be made.

During the preliminary trials it was discovered that changes of temperature caused slight movements in the wood of the box which produced corresponding errors in the adjustment of the mirrors. The trouble was removed by an arrangement whereby any necessary adjustments could be made from outside the box

immediately before readings were taken. A white card placed over the slot of the hemispherical mirror has a hole which is exactly filled by the pencil of radiation when all is in adjustment. The card may be viewed through a window in the side of the box, and any shift of the mirrors is immediately apparent by the streak of light which shows at the edge of the hole. Readjustment is effected with two keys which are pushed through small holes in the side of the box and engage with square section pins on the two controls of the plane mirror. If the box were opened for this operation the uniformity of temperature within it would be destroyed and the thermopile disturbed for some time afterwards.

Radiation from the slit enters the box through a thin glass window W , figure 1, which also serves to prevent low-temperature radiation from the slit-mounting from reaching the thermopile.

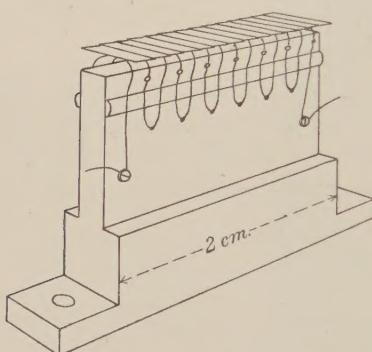


Fig. 3 a. The thermopile.

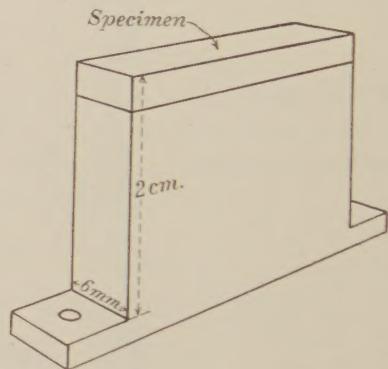


Fig. 3 b. A mounted specimen.

The thermopile. The thermopile used in this investigation differs from that of Coblenz in certain details. Its form will be most readily appreciated from figure 3 a. It is of compact construction, the wires being bent round and anchored so that no part projects beyond the blackened receiving-surface. It can therefore be placed close to the brass block upon which the specimen is mounted.

The receiving-surface is continuous in order that no error may result from a difference of intensity-distribution in the incident image and in that produced by reflection from the hemispherical mirror. To this end Coblenz's method was adopted, small strips of tinfoil being attached to the hot junctions and overlapped slightly like the slats of a venetian blind. Each strip was insulated from its neighbours by shellac and the receiver was blackened when complete. Coblenz's instrument was constructed of 22 silver/bismuth thermocouple elements mounted on an ivory block. Owing to the great difficulty of working with fine bismuth wire, the present instrument has been constructed of copper (46 s.w.g., diameter 0.061 mm.) and constantan (40 s.w.g., diameter 0.122 mm.). For soldering together the fine wires an electrically-heated bent wire was used, and the process was carried out in a pool of Canada balsam. The tinfoil receivers measure 5 mm. by 1.3 mm. by 0.02 mm. and are soldered to the hot junctions. The complete receiver, which measures

5 mm. by 15 mm., embodies 12 elements. The method of assembly is discussed elsewhere*.

In blackening the receiver a thin coat of camphor black suspended in turpentine was applied first and the instrument was finally smoked over the flame of a sperm candle. A copper cooling funnel was used in the last operation to avoid damaging the delicate tinfoil surface. Even when blackened in this manner the thermopile still possessed a reflectivity sufficient to make visible an intense yellow image thrown upon the blackened surface. The error due to incomplete blackness and its correction are discussed later.

The block upon which the thermopile is mounted is of erinoid and is cut away at each side to reduce the total width of the instrument and to minimize the risk of damage to the fine wires. The thermopile is very robust and, in spite of the lower electromotive force of the copper/constantan couple, has proved more sensitive than a similar instrument of bismuth and silver constructed earlier, chiefly owing to its smaller resistance—3·7 ohms as against 15·5 ohms.

The thermopile receiver has an unobstructed view of the whole of the hemispherical mirror. Coblenz's instrument seems to have been shaded from peripheral portions of the mirror by projecting brasswork.

Much disturbance was at first caused in the thermopile circuit by waves of air pressure from closing doors and gusts of wind. This effect has been considerably reduced by inclusion in the circuit within the box of a second exactly similar thermopile, connected in the opposite sense and not exposed to radiation. Impulsive effects in the two thermopiles should then be equal and opposite. Some unsteadiness still remains, however, and has so far prevented the galvanometer from being used with a period greater than 4 seconds.

The galvanometer. The thermopile is connected to a Paschen galvanometer. The instrument is of recent design, and is screened from electromagnetic disturbances by two small shields, one of mumetal and the other of Swedish iron. It is mounted on a brick pier which stands on a separate clay foundation and has proved very free from vibration. The galvanometer lamp has a filament wound in a fine spiral, a direct image of which is cast upon the scale. The lamp and scale are about $1\frac{1}{2}$ metres distant from the galvanometer and the position of the image can easily be read to the nearest millimetre.

The specimens and their mounting. The specimens are mounted upon standard brass blocks, figure 3b, similar to the erinoid block that carries the thermopile, but not cut away at the sides. After being cut roughly to size and ground at the back to a suitable thickness, the specimens are fixed to the blocks with a cellulose cement and their projecting portions are ground away.

In every case the test surface is arranged to be 2 cm. above the projecting lugs by which the blocks are fastened in the apparatus. All surfaces studied then fall into the same vertical plane as the receiver of the thermopile, and one adjustment of the apparatus suffices for the whole series of tests.

The casing of the hemispherical mirror, figure 2, carries an adjustable plate *A*

* H. E. Beckett, *Journ. Sci. Inst.* 6, 169 (1929).

furnished with two screw-operated slides *BB*. The thermopile *T* and specimen *S₁* are inserted through notches in these and are bolted in position. The slides are linked by the sprockets *CC* and chains to a rod which passes through the box and ends in an external control-knob. By this means the incident radiation can be received upon the specimen or the thermopile as desired, when once the relative position of the two slides has been determined. The slide carrying the thermopile is also slotted to accommodate a second specimen *S₂* similar to *S₁* and symmetrical with it about the thermopile.

Each specimen block is provided with a tapped hole in the back into which a handle may be screwed to facilitate insertion and removal. These operations are effected through a small door in the end of the box. A glass panel in the door allows the positions of the slides to be read without opening the box. The plate *A* upon which the slides are mounted can be screwed down upon springs so as to bring the surfaces of the specimen and thermopile into the diametral plane of the hemispherical mirror.

§ 3. THE ADJUSTMENT OF THE APPARATUS

For this purpose the thermopile is replaced by a light coloured specimen which enables the adjustment to be carried out visually. Reference to the thermopile will, however, be made in order to avoid confusion. The relative positions of the slides are first altered until a space of 2 mm. is left between the specimen and the mounting-block of the thermopile. The auxiliary specimen is at the same distance from the thermopile. A bright image of the slit is then allowed to fall on the main specimen and adjustments are made, without alteration of the relative positions of the slides, until a sharply focussed image falling on the centre of the specimen produces a sharp secondary image upon the centre of the thermopile receiver, by reflection in the hemispherical mirror.

It then only remains to determine accurately the working positions of the slides. The thermopile is replaced for this operation and readings are obtained at various slide-settings as the slides are traversed through the expected positions. Owing to the slightly greater sensitivity of the thermopile receiver in its centre line (immediately over the hot junctions) the curves of deflection against slide-setting show maxima from whose positions the correct settings are obtained. The rapid adjustment of the apparatus at any subsequent time is made possible by the white card already described.

§ 4. THE REGIONS OF THE SPECTRUM STUDIED

The solar energy curve extends approximately from 0.3μ to 3.0μ and has been investigated in greatest detail by Abbott and his co-workers. His mean smoothed curve for Washington with the sun at an elevation of 60° has been presented in convenient form by Johansen* and for the present purpose has been adopted as a standard of summer sunshine. The curve becomes more symmetrical when plotted on a frequency scale, and is shown in this form in figure 4.

* E. S. Johansen, *Strahlentherapie*, 6, 45 (1915).

The four filters which have been used were chosen so as to give fairly narrow transmission-bands equally spaced on a frequency scale throughout the solar spectrum. The radiation from the pointolite lamp has been computed from known figures for tungsten*, on the assumption that the temperature of the bead is 2920° K (the manufacturer's figure), and the radiation bands transmitted by the various filters are plotted in figure 4 on various ordinate scales. Filter I consists of Chances' blue-green contrast filter No. 6, 3·3 mm. thick, with their orange contrast filter No. 4, 2·7 mm. thick. The blue-green band transmitted by the first glass is stopped by the second, a single band in the infra-red with energy centred about the wave-length $1\cdot78\mu$ being left. Filter II comprises a 2-cm. water cell, Chances'

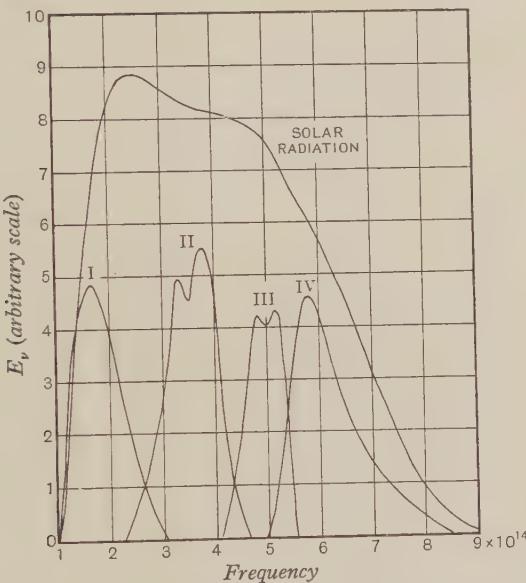


Fig. 4. The radiation transmitted by various filters.

orange contrast filter No. 4 and a cobalt blue glass, 1·8 mm. thick. The blue glass has three transmission-bands. The long-wave band is removed by the water cell and the short-wave band by the orange glass, a band centred at the wave-length $0\cdot84\mu$ being left. Filter III comprises a 1-cm. cell of potassium dichromate solution (72·0 gr. per litre) and a 1-cm. cell of copper sulphate solution (57·0 gr. of the hydrated salt per litre). The transmissions of these solutions overlap slightly and give a band centred at $0\cdot61\mu$. Filter IV is a 2-cm. cell of copper sulphate solution, saturated at $14\cdot2^\circ C.$, which gives a band centred at $0\cdot50\mu$.

The transmissive properties of the above materials in the visible spectrum have been found spectrophotometrically. The infra-red transmissions of the coloured glasses were supplied by the manufacturers, while that of water has been measured by Coblenz†.

* W. E. Forsythe and A. G. Worthing, *Astrophys. Journ.* 61, 146 (1925).

† W. W. Coblenz, *Bull. Bur. Stand.* 7, 619 (1911).

More filters would have been available if the thermopile could have been enclosed in an airtight case, so as to enable the galvanometer to be used at a higher sensitivity. This modification would, however, have entailed the redesigning of the hemispherical mirror-mounting and would have added considerably to the experimental difficulties.

A search has been made for a filter which, in combination with the pointolite lamp, would transmit radiation similar to that of the sun. This would enable the reflecting power of a surface for sunlight to be determined approximately in a single reading.

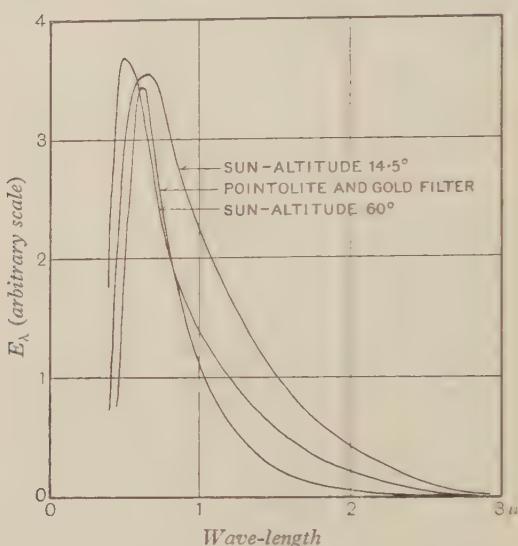


Fig. 5. The radiation transmitted by the gold filter.

The filter finally adopted consists of a thin gold film* sputtered on glass and transmitting 23 per cent. at the wave-length 0.5μ . The curve of transmitted energy, based on the maker's calibration and shown in figure 5, has maximum energy at the wave-length 0.6μ , between the maxima for the high and low sun shown in the same figure. The filtered radiation is somewhat deficient in infra-red energy but yields reflecting powers for solar radiation in fair agreement with those obtained by computation from the results with the other filters. The computed values given in § 6 are based on the energy curve of the sun at 60° elevation.

§ 5. THE CORRECTION OF THE READINGS

In finding the reflecting power of a surface at a particular wave-length two observations are necessary, with the radiation incident upon the specimen and thermopile respectively. The ratio of these readings will be called the apparent reflecting power of the specimen.

* W. W. Coblenz, W. B. Emerson and M. B. Long, *Bull. Bur. Stand.* **14**, 653 (1918).

Certain correcting factors obviously must be applied. Part of the energy diffusely reflected from the specimen is lost through the slot which admits the incident beam, while a further loss occurs by absorption in the hemispherical mirror. Another source of error, which has apparently been neglected by Coblenz and Royds, lies in the incomplete blackness of the thermopile receiver. If the thermopile reflects appreciably and no auxiliary specimen is used, there is an important difference between the optical systems for the two readings. When the radiation falls upon the specimen the thermopile and the specimen lie at conjugate foci of the hemispherical mirror, and any radiation reflected from the thermopile is in part returned to it by subsequent multiple reflections. The thermopile is therefore effectively blacker in this position than in the second, where the radiation is incident directly upon the thermopile and there is no surface at the conjugate focus.

The use of the auxiliary specimen provides similar conditions for the two observations, as will be seen from the following brief analysis.

Let the reflecting powers of the thermopile, the specimen and the silvered mirror for the particular wave-length considered be r_t , r_x and r_s respectively. It will be assumed that the fraction of radiation ($1 - p$) is lost through the mirror slot at each reflection of diffused radiation.

When the radiant energy E falls upon the specimen the reflected radiation is handed backwards and forwards between the specimen and the thermopile in rapidly decreasing amount, and the total energy absorbed by the thermopile is the sum of a geometrical progression and equal to

$$E p r_x r_s (1 - r_t) / (1 - p^2 r_x r_s^2 r_t) \quad \dots\dots(1).$$

Similarly, when the radiation E falls upon the thermopile, the total energy absorbed at its surface is

$$E (1 - r_t) / (1 - p^2 r_x r_s^2 r_t) \quad \dots\dots(2).$$

The ratio of the expressions (1) and (2) gives the apparent reflecting power of the specimen in the simple form

$$p r_x r_s \quad \dots\dots(3),$$

which would obtain if the thermopile were perfectly black and no auxiliary specimen were used.

In the absence of the auxiliary specimen the apparent reflecting power is in the form

$$p r_x r_s / (1 - p^2 r_x r_s^2 r_t) \quad \dots\dots(4),$$

and the quantity r_x cannot be evaluated without a knowledge of r_t .

The assumption of the simple form (3) in this case introduces an error the magnitude of which depends on the various reflecting powers involved. Representative examples are shown in table 1. The error varies linearly with change in the value of r_x .

Tests with blackened specimens show that the reflecting power of the thermopile receiver when freshly smoked is about 0.03, but this value doubtless increases with age.

r_t, r_x, r_s
 p

E

The use of the auxiliary specimen not only renders the observations independent of the blackness of the thermopile but simplifies the correction of other errors.

Table 1. The error caused by reflection from the thermopile.

p	r_x	r_s	r_t	% error in r_x
0.97	0.50	0.98	0.03	1.4
0.97	0.50	0.98	0.05	2.3
0.97	0.50	0.98	0.10	4.5
0.97	0.50	0.85	0.03	1.0
0.97	0.50	0.85	0.05	1.7
0.97	0.50	0.85	0.10	3.4

The value of r_s is readily found by insertion in the apparatus of two glass specimens, surface-silvered at the same time as the hemispherical mirror and subsequently stored beside it in the protecting box. When the incident radiation falls upon the silvered specimen it is reflected specularly and for this reason the factor p is missing from the numerator of expression (1). The apparent reflecting power then gives the value of r_s^2 without further correction. Periodical checking of r_s must be performed in case the mirror tarnishes. Actually the change over a period of 2 years has been found extremely small, not more than 1 per cent. at any wave-length studied. The recent values of r_s for various types of radiation are shown in table 2.

Table 2. The reflecting power of the silver mirror.

Filter	r_s
I	0.977
II	0.940
III	0.915
IV	0.851
Gold film	0.919

For the broad spectral band transmitted by the gold filter it is possible that when the radiation has first been reflected from a highly selective specimen the calibrated value of r_s , namely 0.919, may be somewhat incorrect. Calculation shows, however, that far greater selectivity than that shown by building-materials is necessary to produce appreciable error in this way.

The value of the slot factor p is found by putting in the hemispherical mirror a small blackened screen alongside and of the same area as the slot. With this arrangement apparent reflecting powers are of the form

$$qr_x r_s \dots \dots (5)$$

where

$$q = 2p - 1 \dots \dots (6)$$

and by comparison with the normal values p is readily evaluated.

The factor p must be expected to vary for different specimen surfaces. As, however, the figures obtained for a number of representative surfaces at four wave-lengths all fell within the range 0.96 to 0.98, the standard figure 0.97 has been used

in all determinations of reflecting power. For the greatest accuracy p should, of course, be determined separately for each surface studied. The reflecting powers for magnesium carbonate quoted in the final section are corrected in this manner. The mirror slot is actually bigger than it need be and might well be reduced to one-third of its present area. A standard correcting factor of, say, 0.99 could then be applied with still less possibility of error.

The apparatus is so disposed that radiation specularly reflected from the specimen does not strike the slot.

In the analysis it is assumed that p is constant in the various multiple reflections which occur in the system. This strictly is incorrect but the error introduced is negligible.

There remains the possibility of error due to the dependence of the reflecting powers of the specimen and of the thermopile upon the geometrical distribution of the radiation incident upon them. The greater error is likely to be caused by the thermopile. When total radiation is being measured the incident beam falls normally upon the instrument. In the measurement of reflected radiation, however, the radiation is first diffused by reflection at the specimen, and falls at all angles upon the thermopile receiver. The blackness of the thermopile is likely to be less in this case owing to the increasing reflectivity of the black as grazing incidence is approached. From experiments with a rotatable thermopile it has been calculated that the difference between the reflecting powers of the blackened surface for normally incident radiation and for radiation such as that reflected from a perfect diffuser is about 2 per cent. This is the maximum error to be expected, as rough surfaces which do not obey the cosine law of reflection reflect a smaller proportion of radiation at high angles of incidence.

In the absence of detailed knowledge of the reflecting characteristics of the various specimens, all values of r_x have been multiplied by the full correcting factor 1.02. The correction would be unnecessary for a specimen possessing a large component of specular reflection. In every measurement the mean of six observations has been obtained. The separate observations are read to the nearest millimetre, and zeros are taken as the mean of successive readings to eliminate drift errors. The observational accuracy depends on the size of the deflection measured, and is lowest for surfaces of low reflecting power. The deflection produced when the radiation fell directly upon the thermopile was usually about 40 cm. The reflecting powers in the final section are quoted to the nearest figure in the second decimal place and are likely to be accurate to this figure.

No disturbance due to re-radiation from the specimens has been experienced in this work. An intense beam of radiation thrown for five minutes upon a dark brick specimen, reflecting about 10 per cent., produced no change in a deflection of 21 cm. due to the reflected radiation.

§ 6. RESULTS

The apparatus has been tested with specimens of magnesium carbonate, for which the reflecting power in the visible spectrum seems well established. The specimens were cut from the commercial block form of the material and were about 5 mm. thick. The figures obtained for surfaces prepared with fine glass-paper are shown in table 3, together with all necessary corrections. The high reflectivity found in the visible spectrum agrees closely with the figure 0.981 for white light at normal incidence obtained by McNicholas* at the U.S. Bureau of Standards (probably the most accurate determination yet made).

Table 3. The reflecting power of magnesium carbonate.

	I (1.78 μ)	II (0.84 μ)	III (0.61 μ)	IV (0.50 μ)	Gold film
Apparent reflecting power ($pr_x r_s$)	0.582	0.885	0.854	0.771	0.839
Slot constant (p) ...	0.970	0.969	0.972	0.965	0.970
Silver reflecting power (r_s) ...	0.977	0.940	0.915	0.851	0.919
Obliquity correction ...	1.02	1.02	1.02	1.02	1.02
True reflecting power (r_x) ...	0.63	0.99	0.98	0.96	0.96

Apparently the reflecting power of magnesium carbonate is not constant through the visible spectrum, but rises slightly towards the red.

The tests with blackened surfaces, mentioned previously, showed a reflecting power of 0.03 with all filters except filter I. In this region (1.78 μ) the reflecting power was 0.02. The surfaces were blackened to resemble the receiver of the thermopile, tinfoil being painted with camphor black in turpentine and finally smoked over a sperm candle.

In table 4 are given the reflecting powers of a representative collection of building materials. The figures speak for themselves and need little discussion. One point worthy of note is the low reflectivity for total sunlight shown by almost all roofing materials. The good effect of whitening a roof surface where undue absorption of heat is undesirable is well seen from the results for galvanized iron. An even greater improvement is obtained with darker materials such as asphalt and slate.

§ 7. ACKNOWLEDGMENT

The author wishes to take this opportunity to express his thanks to Mr A. F. Dufton, at whose suggestion this investigation was undertaken and whose assistance and supervision have been most helpful.

* H. J. McNicholas, *Bur. Stand. Journ. Res.* 1, 29 (1928).

Table 4. The reflecting powers of building materials.

No.	Specimen		Reflecting power					
	Description		I (1.78 μ)	II (0.84 μ)	III (0.61 μ)	IV (0.50 μ)	Gold film	Computed
<i>Clay tiles</i>								
29	Dutch: light red	...	0.68	0.66	0.56	0.21	0.57	0.52
31	Machine-made: red	...	0.72	0.42	0.34	0.11	0.38	0.38
25	" red	...	0.55	0.38	0.31	0.11	0.34	0.33
33	" lighter red	...	0.52	0.40	0.32	0.13	0.34	0.33
34	" dark purple	...	0.22	0.22	0.19	0.13	0.19	0.18
28	Hand-made: red	...	0.60	0.47	0.37	0.12	0.40	0.39
24	" red-brown	...	0.55	0.33	0.28	0.13	0.31	0.31
<i>Concrete tiles</i>								
27	Uncoloured	...	0.37	0.38	0.36	0.27	0.35	0.33
32	Brown	...	0.13	0.17	0.15	0.09	0.15	0.13
26	Brown: very rough	...	0.08	0.13	0.13	0.10	0.12	0.11
30	Black	...	0.06	0.09	0.09	0.09	0.09	0.08
<i>Slates</i>								
42	Dark grey: smooth	...	0.09	0.11	0.11	0.09	0.11	0.10
43	" fairly rough	...	0.10	0.11	0.10	0.09	0.10	0.10
46	" rough	...	0.09	0.10	0.11	0.11	0.10	0.10
44	Greenish grey: rough	...	0.16	0.11	0.12	0.13	0.12	0.13
45	Mauve	...	0.14	0.16	0.13	0.10	0.14	0.13
47	Blue-grey	...	0.20	0.16	0.13	0.12	0.13	0.15
48	Silver-grey (Norwegian)	...	0.22	0.21	0.21	0.19	0.21	0.20
<i>Other roofing materials</i>								
1	Asbestos cement: white	...	0.35	0.42	0.41	0.36	0.41	0.39
2	red	...	0.33	0.33	0.29	0.14	0.31	0.26
36	Enamelled steel: white	...	0.35	0.53	0.53	0.57	0.52	0.52
37	" green	...	0.26	0.34	0.17	0.13	0.24	0.25
38	" red	...	0.24	0.26	0.18	0.08	0.19	0.19
39	" blue	...	0.23	0.27	0.17	0.18	0.20	0.23
40	Galvanized iron: new	...	0.58	0.30	0.34	0.34	0.35	0.35
41	" very dirty	...	0.10	0.09	0.09	0.09	0.09	0.09
62	" whitewashed	...	0.63	0.79	0.79	0.76	0.78	0.74
49	Special roofing sheet: brown	...	0.20	0.15	0.12	0.07	0.13	0.13
50	" green	...	0.13	0.20	0.12	0.12	0.14	0.15
8	Bituminous felt	...	0.10	0.12	0.11	0.11	0.12	0.11
60	Aluminized felt	...	0.67	0.60	0.61	0.57	0.62	0.60
59	Weathered asphalt	...	0.12	0.12	0.11	0.09	0.11	0.11
61	Roofing lead: old	...	0.46	0.20	0.19	0.15	0.21	0.23
<i>Bricks</i>								
19	Gault: cream	...	0.74	0.69	0.64	0.43	0.64	0.61
16	Stock: light fawn	...	0.56	0.47	0.38	0.19	0.44	0.39
10	Fletton: light portion	...	0.67	0.61	0.57	0.35	0.58	0.52
9	" dark portion	...	0.54	0.46	0.37	0.15	0.41	0.37
15	Wire cut: red	...	0.56	0.48	0.41	0.15	0.44	0.39
17	Sand-lime: red	...	0.41	0.37	0.30	0.11	0.32	0.30
18	Mottled purple	...	0.33	0.26	0.22	0.15	0.23	0.23
14	Stafford: blue	...	0.21	0.12	0.11	0.08	0.11	0.12
20	Lime-clay (French)	...	0.57	0.63	0.52	0.29	0.54	0.49

DISCUSSION

Dr EZER GRIFFITHS. I wish to congratulate the author on the manner in which he has persevered to overcome the numerous difficulties in the technique of this class of work. There is one question I would like to ask him: Would it be possible to modify the apparatus so as to obtain average values for areas of the order of 1 ft.² or so? In studying commercial materials such as building-bricks and roofing-tiles it is desirable to obtain average values for a number of samples, owing to the heterogeneous nature of the materials. To obtain the necessary data from test surfaces of very small area would involve much labour.

DR J. H. COSTE said that it would be a pity if such a good piece of work were to be spoilt by lack of sufficiently varied data. It would be useful if a great many specimens of each material could be examined: an idea of the variability of the material could be obtained in this way.

Mr J. GUILD. The author is to be congratulated on the care and ingenuity with which he has eliminated the various systematic errors to which the measurements are liable on account of incomplete reflecting power of the silver mirror, incomplete absorption by the thermopile, etc. In the latter connexion, has he had an opportunity of trying bismuth black, recently recommended by Pfund as having a considerably higher absorption-coefficient than the blacks usually employed on thermopiles? With regard to the check measurements on magnesium carbonate, I do not think it is quite correct at the present time to regard this as the material of which the constants are best known. A recent paper by Preston in the *Transactions of the Optical Society* gives values for magnesium oxide which are probably more reliable than any that exist for magnesium carbonate. If the oxide is smoked on to a silver surface no great thickness of deposit is necessary to obtain constant properties.

The author could, apparently, make use of greater sensitivity than he obtains at present, were it not for the disturbing effects of draughts and adiabatic pressure-waves affecting his thermopile. I suggest that these effects could be greatly reduced in one or both of two ways. If the mounting which carries the thermopile and specimens were constructed to close completely the hemispherical mirror, and a window of thin glass or mica were placed over the slot in this mirror, the pile would be protected from the air currents which inevitably circulate in the larger box. The second improvement is on the lines which the author has already utilized in principle, namely the connexion in opposition to the main thermopile of another similar pile not exposed to the radiation. In order to obtain much advantage from this mode of compensation it is, however, necessary for the two piles to be in close juxtaposition, so that any local eddies may affect them to similar extents.

It would not be possible, without destroying the symmetry which is essential in the author's system, to mount one pile beside the other, as is done in an apparatus described by me in the January number of the *Journal of Scientific Instruments*, but a very satisfactory alternative would be to make the compensating pile in two

portions, one at each end of the main pile, on the same mount. If this were done, in addition to restricting the space by closing up the spherical mirror, it is probable that the air-disturbance effects would be negligible at the highest sensitivity of which the galvanometer is capable. The difficulty of hermetically sealing the space within the spherical mirror without interfering with the lateral adjustment of the thermopile and specimens could readily be overcome by allowing the back plate to slide over a flange on the mirror mount and sealing the joint with vaseline or a light tap grease.

A secondary advantage which would accrue from enclosing the spherical mirror would be a further reduction in its rate of tarnishing.

Dr J. S. G. THOMAS enquired whether it was correct to refer to the *reflecting* power of the specimens as what was measured. Should it not rather be the *scattering* power of the specimen? He also enquired whether the data contained in table 4 could not be set out in such manner as to be of more immediate use to architects and builders, more especially in regard to the specification of the materials and the arrangement of the specimens in the different classes in either ascending or descending order of scattering power.

AUTHOR's reply. I agree with Dr Griffiths that the use of larger specimen surfaces is desirable where average values are required. With Coblentz's method the use of a small specimen is unavoidable. Had any other method capable of dealing with larger surfaces appeared practicable it would certainly have been adopted. With every material as representative a sample as possible has been selected. Where great variability occurs it may be necessary to repeat measurements with a number of samples.

In reply to Mr Guild: My apparatus was working satisfactorily when Pfund's paper relating to bismuth black appeared, hence I have not tried a thermopile blackened in this way. I considered magnesium oxide for the purpose of check measurements but rejected it in favour of the carbonate. Preliminary tests showed that the oxide had to be used in a considerable thickness in order to yield repeatable results, and that, moreover, its reflecting power was subject to a slight change due to carbonation. The thermopile could doubtless have been steadied still further by boxing-in of the hemispherical mirror. As, however, the use of the compensating thermopile had reduced the disturbances sufficiently for the tests in hand, such a change in design, which could not have failed to have made the apparatus more difficult to adjust and handle, was not embarked upon.

The term "scattering power" suggested in preference to "reflecting power" by Dr Thomas, is not, I think, applicable to the quantity which I have measured. For the ratio of the total reflected radiation to the total incident radiation "reflecting power" is surely correct, even where the reflection is not specular.

The information given in table 4 is of minor importance in a scientific paper dealing essentially with the method of measurement. The results will be published by the Building Research Station in a form more suitable for the attention of architects and builders.

THE VELOCITY OF SOUND-WAVES IN A TUBE

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ABSTRACT. The apparent velocity of sound in a tube of diameter 2 cm. has been measured at temperatures up to 400° C. and with frequencies of from 3000 to 14,000 ~. The reduction in velocity below the free-air value is discussed, and the suggestion is put forward that this reduction, for a single tube and gas, depends on the wave-length rather than on the frequency. The theoretical expression found by Helmholtz and Kirchhoff for the reduction in velocity does not appear to be valid, at any rate for the conditions obtaining in these experiments. The method used by Dixon and by Partington and Shilling for correcting for the influence of the tube receives support from the present results.

The experiments reveal the complication which ensues when the wave-length falls below a certain multiple of the tube diameter.

§ I. INTRODUCTION

RATHER more than sixty years ago, Helmholtz and Kirchhoff investigated theoretically the reduction in velocity suffered by plane waves of sound advancing along a narrow tube. The former author considered only the effect of the viscosity of the air, whilst Kirchhoff took into account also the effects of thermal conduction, but both reached a formula which may be written

$$V = V_0 (1 - A/r\sqrt{n}) \quad \dots \dots (1),$$

*V, V_0 , r
n, A
B*

where V is the velocity in the tube, V_0 is the velocity in free air, r the radius of the tube, n the frequency and A is a constant with different meanings in the two investigations, but in any case depending on the gas and on the material of the tube. In the intervening years the equation of Helmholtz and Kirchhoff has been studied by numerous observers, some of whom find it correct, although several report that the observations agree better with a formula $V = V_0 (1 - B/m^{\frac{1}{3}})$.

The purpose of the present paper is to investigate the velocity-reduction afresh. The whole of the observations were carried out with one tube and with pure dry air as the gas, so that no complications arose owing to variations in the roughness, etc. of the tube walls. The velocity was obtained by direct measurement of the internodal distance when standing waves were set up in the tube. The frequency was varied over a large range of values, and measurements were carried out at four temperatures, 14° C., 163° C., 320° C. and 424° C.

The observations brought out incidentally the fact that no simple formula can deal with waves of all frequencies in a given tube. This seems to be connected

with a phenomenon pointed out by Rayleigh,* who showed that waves set up in a cylindrical tube will ultimately become plane, provided that the frequency is less than that of the natural transverse vibration of the tube, i.e. if the wave-length exceeds 3·4 times the radius. Otherwise, the sound pattern is immensely complicated by the transverse waves, and the apparent internodal distance is liable to error.

§ 2. DESCRIPTION OF APPARATUS

The apparatus is shown in figure 1. It consists of a furnace-tube of pyrex glass of internal diameter 2·0 cm. and wall-thickness 0·20 cm., a listening-tube being attached near one of its ends and a movable reflector supported inside it. The source of sound is situated beyond the end of the furnace-tube remote from the reflector,

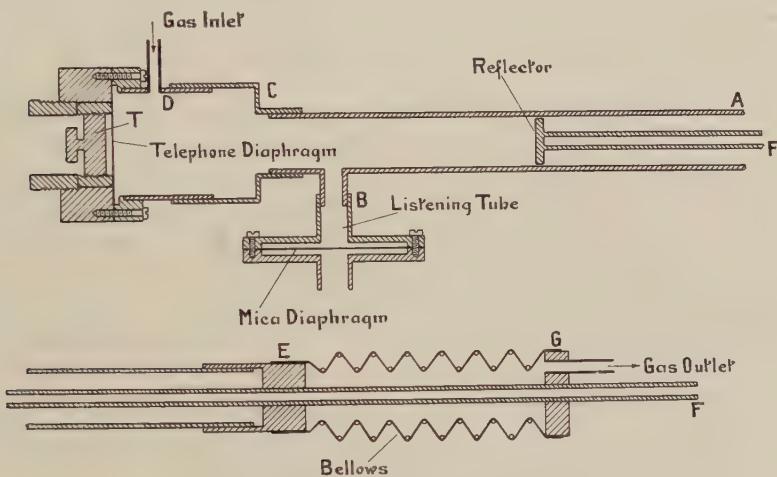


Fig. 1. Sectional view of apparatus.

and before observations are made, the distance between the telephone and the side tube is adjusted until maximum sharpness of the nodes is reached. Successive nodes can then be brought under the listening-tube by movement of the reflector; the internodal distance is directly measured from this movement.

On reference again to figure 1, it will be seen that on the side tube is fixed a brass mounting carrying a 5·0-cm. mica diaphragm of thickness 0·003 cm. This is to prevent the escape of gas and still allow the passage of sound. On the same end of the furnace-tube is fastened a brass collar and flange carrying a brass tube *C* of internal diameter 5·3 cm. and wall-thickness 0·6 mm.

The telephone *T* is mounted in a brass case carried by a brass tube *D* which makes a sliding fit inside tube *C*. Tube *D*, of the same material as *C*, carries the inlet gas-tube, which is branched to communicate with the outside air. To render the tubes gas-tight, a rubber tube of slightly smaller diameter than tubes *C* and *D* is stretched over them. One end of the rubber tube is cemented on to tube *C*

* *Theory of Sound*, 2, § 301, p. 161 (1894).

and the other on to tube *D*. This allows free movement of one tube within the other, while preventing the entrance or escape of gas. The telephone used is a Brown A earpiece with ebonite cap and cone removed. The construction of the telephone-mounting and the method of stretching the steel diaphragm can be seen from the figure. On the other end of the furnace-tube is a brass collar *E* drilled with a central hole of diameter 9 mm. This supports a pyrex tube *F* carrying the *Pt-Pt-Rh* thermocouple with which the temperature is read, and has on its end a solid pyrex disc, making a loose fit in the tube. It is about 3 mm. thick except in the centre, where it is thinner to allow of the close approach of the thermo-junction to the face of the disc.

The other end of the movable tube is supported in a wooden block fixed to a cursor engraved with a fine line, and sliding along a steel metre rule. Close to its end support, tube *F* carries a brass disc *G* which is drilled to take the exit gas-tube. Between the collar *E* and the disc *G* and fitting tightly on to both is a rubber bellows to obviate the use of a packing gland.

A steel tube of length about 2 ft. 6 in. and of slightly larger diameter than tube *A* constitutes the furnace. It is wound with nichrome wire, the turns being more widely spaced in the centre, to give a more uniform temperature-distribution. There is uniformity of temperature to within $\pm 1^\circ \text{C}$. at 500°C . over a central length of about 30 cm. The temperature was measured at three points in this region before and after every experiment.

The whole apparatus is mounted on an optical V-bench, separate supports being used for the telephone, furnace and metre rule, and the various parts being accurately aligned.

The gas used in these experiments is dry air, free from CO_2 . It is passed through three wash-bottles containing strong sulphuric acid and through two others containing a saturated solution of caustic potash. It then passes through tubes of calcium chloride and phosphorus pentoxide into the apparatus via tube *D*. A mercury manometer is included in the circuit, one arm being open to the atmosphere. A pressure of about 6 cm. of mercury is required to send a slow stream of air through the apparatus, on account of the air having to pass between the collar *E* and the pyrex tube *F*. This collar is made to have a close fit, to prevent the motion of cold air into the hot region when the bellows are compressed. At the exit end the gas is led from tube *G* into a spherical glass vessel 30 cm. in diameter, containing calcium chloride, and from this it passes to a wash bottle containing sulphuric acid. The effect of this sphere (which is not shown in the figure) is to minimize the changes in pressure caused by movement of the bellows.

To dry the furnace tube, the temperature was raised to about 600°C . and air was passed through it. The bellows were heated from the outside by means of a stream of hot air to prevent the deposition of moisture. The moisture was thus driven out into the large glass sphere where it was absorbed by the calcium chloride. This process was continued till no more moisture was deposited in the sphere. The internal pressure can at any time be reduced to atmospheric by momentarily opening the tap on tube *D* and allowing excess gas to escape.

§ 3. OSCILLATOR

The chief features of the oscillator are the number of different frequencies obtainable and their extreme constancy. It is in two stages:

(a) *A crystal-controlled multivibrator.* This consists of an oscillating circuit with a quartz crystal between grid and filament, coupled to an Abraham-Bloch multivibrator. The latter circuit is very unstable and very rich in harmonics and the crystal exercises its control through one of these harmonics. The arrangement is shown in figure 2. It was found that, by a suitable choice of the inductance L_1 , the capacity C_1 could be dispensed with and the circuit would still oscillate quite readily. Also the condenser C_2 was replaced by two fixed $0.001\text{-}\mu\text{F}$ condensers which could be coupled in series or in parallel. The different sub-harmonics of the crystal frequency were then obtained by variation of C_3 alone. They are far enough apart to be easily identifiable. The crystal used had a natural frequency

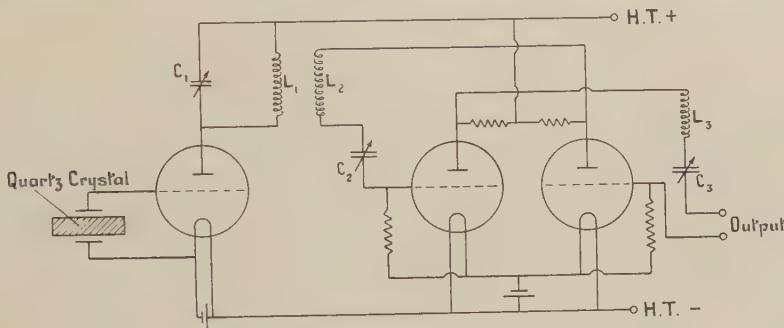


Fig. 2. Crystal-controlled multivibrator.

of $27,422 \sim$ and dimensions $10 \times 1 \times 1 \text{ cm}$. The frequency was measured with the crystal mounted exactly as in the following experiments, and it was verified that the switching on or off of the multivibrator or the variation of condenser C_3 made absolutely no difference to its frequency. A previous measurement, some weeks before, when the crystal was in a different mounting, had given the value $27,423 \sim$ and indicated a negative temperature-coefficient of frequency of about 1 part in 10^6 per ${}^\circ\text{C}$.

(b) *A two-stage amplifier.* The amplifier is of conventional design, two AF5 Ferranti transformers being used. This was quite satisfactory when the higher notes were being used, but for the lower ones a difficulty was encountered, due to the presence of the overtones of the fundamental. The procedure eventually adopted when one of the lower notes was required was to replace the two Ferranti transformers by two comparatively inefficient ones. Also the telephone diaphragm was relieved of all tension and its response to high notes was thereby weakened. By these means a note free from overtones could be obtained. On the other hand, if such a frequency as $4/13$ of the crystal frequency were required, the two Ferranti transformers were retained and the multivibrator was tuned to $1/13$ of the crystal

frequency. If the crystal frequency be denoted by N , the telephone would then be emitting a fundamental note of frequency $N/13$ together with some of the overtones, i.e. notes of frequency $2N/13$, $3N/13$, etc. It was sometimes possible so to magnify one of these overtones, by tuning the telephone diaphragm to the correct frequency, that the other notes were hardly audible by comparison. In this way frequencies such as $2/5$, $2/7$, $3/7$ and $3/10$ of the crystal frequency were obtained and used in experiments. A rheostat is included in the filament circuit of the amplifier, so that when the maxima have been obtained sharply and distinctly, the volume of the sound can be diminished, until nothing at all is audible in the side-tube except over a very small range on either side of a maximum. In the case of the high notes, this range could be reduced with care to about 0.5 mm. In the taking of measurements, each maximum was approached from both sides, and the mean position was taken. Several pairs of readings were taken for each maximum. Attention was paid principally to the maxima at each end of the uniform temperature region, the intermediate maxima being measured only once, chiefly as a check on their equidistance.

§ 4. RESULTS. REDUCTION TO FREE-AIR VELOCITIES

As has been previously stated, the internodal distance was measured at a number of frequencies at each of four temperatures. From the internodal distance (i.e. the half-wave-length) the velocity of the sound under the particular conditions

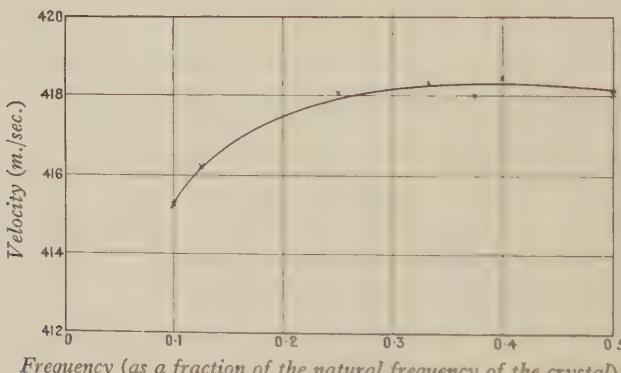


Fig. 3. Sound-velocity as a function of frequency at 163° C.

concerned is immediately obtained as the product of wave-length, λ , and frequency n . Even at one temperature and in one tube these velocities are not absolutely constant, because each is reduced below the free-air value by an amount varying with the frequency. The results at 163° C. are shown in figure 3 as an example. Regarded as a function of frequency the velocity appears to pass through a maximum, although the fall is hardly sufficient to establish the fact with certainty. It is, however, supported by a similar variation in the graphs for each of the other three temperatures.

The object is to find from these observations the true free-air velocity at each of the four temperatures and, if possible, to establish the correct form of the law governing the reduction in velocity.

Method (1). A natural method for calculating V_0 , and one which has been used by several of the early observers, is to use the observations to deduce the constant A in the Helmholtz-Kirchhoff formula quoted above. We have adopted this method, using, however, a generalized formula $V = V_0(1 - B/r^x)$, where B will in general depend on r , the radius of the tube.

The constants V_0 , B and x were obtained from three values selected from below the maximum on a smoothed curve such as that shown in figure 3.

The results found are set out in table 1.

Table 1.

Temperature	x	B	V_0 (m./sec.)
14° C.	1.92	0.00008	339.7
163	1.41	0.00038	419.2
320	1.26	0.00052	487.2
424	0.49	0.0063	532.7

There is no evidence that the power x is in general either 0.5, as in the theory, or 1.5 as certain observers have reported, although it may well occur that one or other of the values would be found under special conditions. In so far as they provide a basis for a general method of correction, the observations indicate that x decreases rather rapidly with increasing temperature, and that B increases even faster. Thus the Helmholtz-Kirchhoff law would appear to have no general validity, even with slight modifications of form.

Method (2). A somewhat different method of correcting the observations to obtain free-air values has been used by Dixon* and by Partington and Shilling† in their extensive work on the specific heat of gases. In this method the Helmholtz-Kirchhoff equation is again taken as a basis, but modified in a different manner from that just suggested in method (1).

Kirchhoff's theoretical value being adopted for the constant A , equation (1) becomes

$$V = V_0 \{1 - [\mu^{\frac{1}{2}} + \nu^{\frac{1}{2}} \gamma^{-\frac{1}{2}} (\gamma - 1)] / 2r\sqrt{(\pi n)}\} \quad \dots\dots (2),$$

where

μ is the kinematic viscosity,

γ is the ratio of the specific heats,

ν is the thermal diffusivity of the gas.

and

Dixon writes this in the form $V = V_0(1 - kc)$, where c is the numerator in the above fraction, and k^{-1} is theoretically $2r\sqrt{(\pi n)}$. Accepting the theoretical value for c , he obtains an empirical value for k from an accurate experiment with a gas for which V_0 is accurately known at the temperature of the experiment. This k is then

* Proc. R. S. A., 100, 1 (1921).

† The Specific Heats of Gases, p. 53 (London, E. Benn, Ltd., 1924).

regarded as a constant associated always with the particular tube and frequency. The value of c is taken from the formula, and regarded as a function of temperature for the particular gas. For experiments at other temperatures, or with other gases, the observed velocity is corrected by division by the factor $(1 - kc)$, with the above value of k and with the appropriate value of c . No particular justification is given for the assumption that k does not vary with temperature nor with the gas used.

The data obtained in the present work were corrected by this method. From the smoothed curves of velocity against frequency, values were read off at frequencies 13711, 6856 and 4570 ~. The value at 14° C. was taken (from the work of other observers) to be 339·8 m. sec. Thus at any one of the frequencies mentioned, V as observed = $339\cdot8(1 - kc)$, where c is known, so that k can be evaluated. The values found for k were 0·00328, 0·00246 and 0·00492 for the three frequencies mentioned. It is to be remarked that at all temperatures the last two frequencies fall to the left of the maximum on the velocity frequency curve, and the first one falls to the right.

With these values of k , and the appropriate c for each temperature, the corrected velocities found were as shown in table 2.

Table 2.

Temperature (C.)	14°	163°	320°	424°
Frequency 13711 ~	339·8*	419·2	487·6	529·0
6856 ~	339·8*	418·85	487·1	527·3
4570 ~	339·8*	418·7	487·4	527·4

* Assumed value.

It appears that by this method of correction the results taken at the highest frequency (i.e. beyond the maximum of the frequency velocity curve) are definitely high, but for the other two frequencies the results show no significant variation with frequency.

§ 5. GENERAL DISCUSSION OF THE CORRECTION

The only assistance which theory gives in evaluating the tube correction is that afforded by the Helmholtz-Kirchhoff formula. Both methods of correction which have been described in the paper are based on modifications of that formula. If the correct free-air velocities were known it would be possible to evaluate the actual corrections and to discuss the laws which they follow, but it is obviously impossible to conduct experiments in free air at these temperatures, so that the true values have to be obtained from the observations in a tube. Even if the methods used are regarded as empirical, it is likely that where they agree in giving the same estimate of the free-air velocity this must be substantially accurate. Table 3 shows the agreement between the two methods, the values obtained at the highest frequency, where the waves are probably not plane, being rejected.

True open-air values (independently of any correction) have been determined for sound at air temperature by Hebb and others, and we may take the correct value at 14°C . to be 339·8 m./sec. At temperatures of 163° and 320°C . our corrected values by the two methods are in substantial agreement, with mean values of 418·9 and 487·2 m./sec. respectively.

Table 3. Corrected values of velocity (m./sec.).

Temperature $^{\circ}\text{C}.$	Method (1)	Method (2)	
		Frequency 6856 ~	Frequency 4570 ~
14	339·7	—	—
163	419·2	418·85	418·7
320	487·2	487·1	487·4
424	532·7	527·3	527·4

Adopting these values, but setting aside for the present the values at 424°C . on the ground that the true value is not defined with sufficient accuracy, we have calculated the difference between each observation and the free-air value at the same temperature. On examination of the law followed by these corrections, it appeared probable that the percentage reduction in velocity was more likely to be related to the wave-length than to the frequency, since then the wave pattern is likely to be unaltered. It is true that at a fixed temperature the substitution of one for the other is immaterial, but this is not so when the temperature is allowed to vary. Moreover, the evidence from the calculations of method (1) shows that there is no simple law, valid for all temperatures, connecting velocity-reduction with frequency.

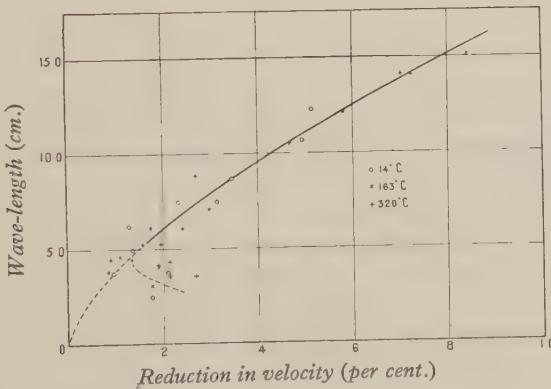


Fig. 4. Percentage reduction in velocity as function of wave-length.

Accordingly, the corrections expressed as percentages of the corrected velocity have been plotted against the wave-length in figure 4. The points for each temperature are shown separately, and it will be observed that the points for all temperatures lie on one curve. This curve shows in the lower left-hand corner a large irregular group of points which correspond to the points at and beyond the maximum of

the velocity/frequency curve, where the waves are probably not plane. The general course of the curve is doubtless somewhat as shown in the right-hand dotted line, figure 4, and must be due to a failure of the ordinary theory of sound-propagation when the wave-length is too small. Rayleigh has in fact pointed out that the wave will ultimately become plane if the wave-length exceeds 3·4 times the radius, and although he did not investigate the motion for wave-lengths shorter than this, we assume, as was remarked in the introduction, that transverse waves would exist and introduce subsidiary nodes. The numerical agreement with Rayleigh's result is not exact, for the minimum reduction of velocity in figure 4 occurs when the ratio of wave-length to radius is about 4·5, i.e. somewhat greater than the theoretical figure. It would hardly be expected that the transition to plane waves would be completed in a negligible distance, until the ratio exceeds 3·4 by some substantial amount, a fact which is implied in Rayleigh's investigation*.

Returning to consideration of the remainder of the curve, which, it will be seen, is well defined, we note that there appears to be no effect of temperature greater than the experimental error. The corrections follow approximately a 1·5-power law of the wave-length, and the curve drawn represents in fact the law

$$\text{percentage error} = 0.0136 \lambda^{1.5}.$$

As far as we are aware, this suggestion that wave-length is the true criterion has not previously been put forward. It will of course require further experimental work, both over more extended ranges of temperature and with tubes of other materials and of different diameters. Should it be substantiated, however, it opens up a new method of applying the correction for the reduction of the velocity of sound in a tube. The apparent velocity having been determined at a temperature where the true velocity is known, the constant in the law

$$\text{percentage error} = \text{constant} \times \lambda^{1.5}$$

is known, and all observations with this tube can be corrected by this law, whatever the temperature. It may be, however, that the particular form of the law found by us is incidental to the experimental arrangements adopted. In this event it would be necessary to determine the whole of the λ error curve by experiments at different frequencies, but the method would still have the advantage of allowing these experiments to be carried out at some convenient temperature. It would be necessary, of course, to know the true value at that temperature, however it may be derived.

An interesting test of the suggested law is to apply it to our observations at 424° C. which were not used in computing the λ error curve. The results found are shown in table 4.

The corrected values show no systematic variation with wave-length, and the mean value is 527·6 m./sec. This agrees well with the value 527·4 obtained from the same data by method (2), and suggests that the use of that method is not liable to cause serious error.

* *Loc. cit.* p. 161; equation (12).

Table 4.

Wave-length (cm.)	Uncorrected velocity (m./sec.)	Corrected velocity (m./sec.)
15·27	523·4	527·7
11·47	524·3	527·1
9·59	525·7	527·9
7·67	525·8	527·3
5·76	526·9	527·9
4·80	526·9	527·6
3·84	527·1	527·6

§ 6. ACKNOWLEDGMENTS

We have to thank Dr G. W. C. Kaye, Superintendent of the Physics Department, for his interest and the facilities for carrying out this work. For the crystal used we have to thank Dr Dye, whose continued interest has been most helpful on many occasions. Mr A. R. Challoner, Observer, constructed practically the whole apparatus and contributed materially to the design, particularly as regards the mounting of the telephone diaphragm.

DISCUSSION

Dr A. B. Wood referred to the high degree of precision attained in the measurement of the velocity of sound to 1 part in 4000. He pointed out, however, that the amplitude of movement of the particles might amount to 1 or 2 mm. and their velocity to 1 or 2 m./sec. It might be well, therefore, if the authors would state the exact figures for these quantities and indicate any allowance made for them. Peirce, in the course of an investigation carried out by means of the quartz oscillator, ascribed to changes of frequency the variations which he observed in the apparent velocity of sound. These variations might be more easily explicable, however, as due to the effects of particle-velocity.

Mr N. FLEMING. The authors state in their introduction that "the velocity was obtained by direct measurement of the internodal distance when standing waves were set up in the tube." If I understand their procedure correctly, this statement is not strictly accurate. The internodal distance was inferred from measurements of the displacements of the piston which were necessary to give a succession of nodes at the listening-tube. The point is of some importance, for if they had measured directly the distance between nodes they would have avoided one of the possible sources of error in their method; this is the error which may arise through imperfect reflection of sound at the piston, due both to leakage of sound round the piston (which makes only a loose fit in the tube) and to longitudinal vibration of the free portion of the piston-rod. I see that Mr Henry has treated both these points

in his paper, but it may be of interest to consider qualitatively the variation with frequency of the error due to the latter cause. If reflection from the piston is not perfect, i.e. if the terminating impedance of the tube is not infinite, there may be a shift in the position of the whole nodal system, though the distance between nodes remains unaltered. The magnitude and direction of this shift vary with the terminal impedance and so with the free length of the piston-rod. Figure 1 of Mr Henry's paper illustrates the variation of the shift with l/λ' , the ratio of the free length of the piston-rod to the wave-length of longitudinal vibrations in it, negative values corresponding to a shift towards the piston. For a low frequency and a small value of $l/l\lambda'$ is small and there is a slight shift of the nodes towards the piston. As the piston is moved towards the listening-tube l/λ' increases and the shift increases. Consequently the piston must be moved through a greater distance than would be required in the absence of such a shift, and the velocity deduced is slightly too great. At a somewhat higher frequency the difference in the shifts at the two positions is greater. It is true that this error is now distributed over a greater number of internodal distances, but this number does not increase with frequency as rapidly as does the error. The velocities inferred therefore increase at first too rapidly with frequency. At some still higher frequency the free length of the piston-rod may pass through the value $\lambda'/4$ between the two positions at which measurements are taken. The shift in the first position is then towards and in the second position away from the piston. The error is reversed in sign and the velocity deduced is too low. Do the authors consider that such an effect could account for the maximum which they obtain in the variation of velocity with frequency? Can they give any information as to the natural frequencies of the free lengths of the piston-rod used by them?

Mr D. A. OLIVER. I should like to refer to some of the practical points in the authors' apparatus. Is the diameter of the side-tube *B* in figure 1 to scale? If so, it would appear that the acoustical impedance of the main tube at this place would be profoundly modified at some frequencies by the presence of this coupled subsidiary acoustical system, which conceivably might affect, by a measurable amount, the standing-wave system in the main tube. I would suggest that the diameter of this tube should not exceed 1 mm., but any effect due to this cause can easily be checked experimentally.

In a precise discussion of the errors to which tube measurements are subject, would the authors agree that the source and air column could, with advantage, be treated as a coupled mechanical-acoustical system, and the conditions for resonance, involving the mechanical impedance of the source in the correction terms, deduced? The type of source used by the authors is likely to have a mechanical impedance very variable with frequency. An air-damped electrostatic source would be much more uniform with respect to variation of impedance with frequency. As has already been pointed out by Mr N. Fleming, the movable piston also must be taken into account, and I would add, from my own experience, that little or nothing can be assumed to be rigid at frequencies ranging between 3000 and 30,000~.

Dr D. OWEN. It is interesting to note the high accuracy of setting of the piston, in view of the large opening to the listening tube. Is not the accuracy dependent on the frequency, since the intensity of the disturbance is likely to be different at the different frequencies, and the sensitivity of the ear itself varies with the frequency?

Mr P. S. H. HENRY. Is there any evidence of the wave-length readings becoming definite again if the frequency is increased beyond the point at which the readings become indefinite? This would probably be the case if radial resonance were the cause of the variations; for radial resonance would be but little damped, and would only have a serious effect in the neighbourhood of certain definite frequencies corresponding to the various modes of radial vibration of the gas.

AUTHORS' reply. In reply to Dr Wood and Dr Owen, we would point out that the intensity was definitely reduced to such a point that no sound was audible except over a small range in the immediate neighbourhood of a maximum. To reduce the range to a minimum, the telephone had to be carefully adjusted with respect to the side-tube. With alternate reduction of the intensity and adjustment of the telephone, the range of audibility could be greatly reduced. It was, of course, smaller with the higher frequencies. Remembering that Rayleigh has found that amplitudes as small as 10^{-8} cm. give audible notes, we do not think that there can be any difficulty in this direction.

The point referred to by Mr Fleming is of great interest. We are unable to give the frequency of the longitudinal vibrations in the reflector, if only for the reason that the latter could not be regarded as rigidly clamped by the collar *E*. In any case it is clear that vibrations in the reflector cannot appreciably affect the average result determined with a number of different frequencies. It is, however, just possible that they are responsible for the maximum in one of the velocity/frequency curves, in which case the maxima in the remaining curves would be unlikely to be due to the same cause, occurring as they do at about the same wave-length at all temperatures. We agree with him and with Mr Oliver that the system can be regarded as a coupled mechanical-acoustical system and, indeed, would obviously have to be regarded as such if the position of the nodes with respect to the telephone were of importance. It is, however, the internodal distance which is measured, and if the region over which the reflector is moved is far enough from the side-tube, then only a negligible error will be introduced by having the side-tube of large diameter. The diameter in our case was approximately 4 mm.

In reply to Mr Henry, we regret that it was impossible to trace the wave-length error curve beyond the point reached in figure 4.

A BALLISTIC RECORDER FOR SMALL ELECTRIC CURRENTS

By E. B. MOSS, B.Sc.

Received November 21, 1930, and in amended form December 11, 1930.

Read and discussed February 6, 1931.

ABSTRACT. The standard thread recorder is so modified that it records ballistic throws in place of the usual steady deflection. By this means the current-sensitivity may be increased at least twenty-five times.

§ 1. INTRODUCTION

ROBUST and comparatively simple instruments are readily available for the purpose of recording graphically currents greater than $1\mu\text{A}$, and it is when currents of smaller magnitude are to be studied that recourse must be had to elaborate apparatus. Either a photographic method is employed in conjunction with a mirror galvanometer, or the current is amplified, for example with a thermionic valve, and then recorded on a suitable instrument. Any elaboration such as this cannot but reduce the degree of accuracy which may be obtained, and the following paragraphs describe a modification of the standard thread recorder of the Cambridge Instrument Company, whereby this instrument is made to record currents of the order of 10^{-7} amp.

§ 2. DESCRIPTION

Although the thread recorder must be a familiar instrument to many, a brief résumé of its operation may not be out of place here.

The galvanometer coil is freely suspended and the pointer moves above the clock-driven drum carrying the chart. A little above the pointer and parallel to the drum-axis is a chopper-bar, while just below the pointer, i.e. between the pointer and the drum, an inked thread is stretched under slight tension. At half- or one-minute intervals the chopper-bar is released, falling on to the pointer and pressing it down momentarily, with the inked thread, on to the chart. The dot which results on the chart is therefore a register of the pointer-deflection when the chopper-bar fell.

As the title implies, the modified recorder operates on a ballistic principle and some additions are made to the sequence of events detailed above. The circuit used in conjunction with the instrument and shown in figure 1 is not in any sense novel and is that generally employed for measuring small currents ballistically, although its particular application to photoelectric measurements has been mentioned by P. Selényi*. The circuit includes three contacts, *A*, *B* and *C*. While *B* and *C* are

* *Photoelectric Cells and their Application*, p. 41 (The Physical and Optical Societies, 1930).

closed the galvanometer coil is short-circuited and therefore damped. During this time the photoelectric current charges the condenser so that when *B* is moved over into contact with *A* and away from *C* a ballistic impulse is imparted to the galvanometer, and it is the resultant throw that is recorded in place of the usual steady deflection.

The standard thread recorder has the coil wound on a copper former and, with a coil of 2000 ohms' resistance, the current required to produce a full-scale deflection is about 5.0×10^{-6} amp. Such an instrument has a ballistic sensitivity of 24 microcoulombs for the same deflection. This charge accumulating during 60 seconds is equivalent to a steady current of 0.4×10^{-6} amp. Therefore, to use this instrument ballistically increases the current sensitivity 12.5 times. If the time interval between successive contacts is increased the current sensitivity will go up proportionally.

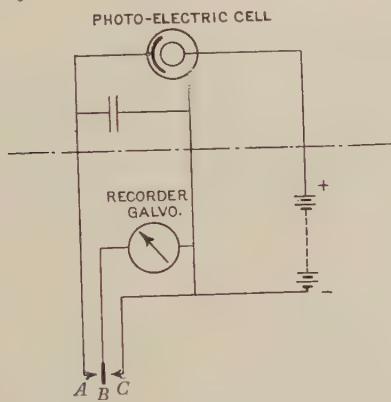


Fig. 1. The electrical circuit.

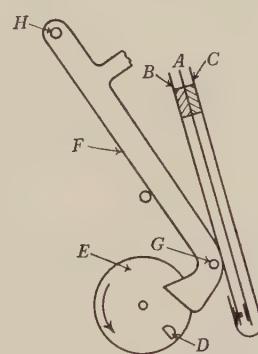


Fig. 2. Contact arrangement.

The movements of the suspended coil are damped almost critically by the copper former, so that an improvement results from its removal; in fact it is found that only 12 microcoulombs are necessary to give a full-scale deflection with a formerless coil. This coil, being undamped, does not return slowly to zero after being released by the chopper-bar, but oscillates about the zero position and would not come to rest during the succeeding minute unless some damping were provided, and it is for this purpose that contact *C* in figure 1 is employed.

The mechanical details are illustrated in figure 2. In accordance with standard practice the cam *E* carries the pin *D* and rotates in the direction indicated by the arrow. In the course of its rotation the pin raises the release arm *F* (which is pivoted at *H* and is subsequently permitted to drop back into its rest position) releasing the chopper-bar so that it falls on to the pointer. Having been released, the chopper-bar is raised by auxiliary clockwork during the course of one or two seconds. The additions to the recorder are the spring contacts, *A*, *B* and *C* which correspond to those bearing the same letters in figure 1. While the condenser is charging, which in practice is for about 56 seconds during each period of one minute, contacts *B*

and C are closed, short-circuiting the galvanometer and damping its movements. As F is raised by the rotation of the cam E the insulated pin G , on the former, presses B out of contact with C , leaving the galvanometer undamped, and then moves B further and into contact with A , thus connecting the galvanometer to the condenser. A ballistic throw results, but E has still to rotate a little before D releases the arm F , and during this time the galvanometer-pointer is travelling to the maximum extent of its throw. The interval is therefore adjusted so that the chopper-bar falls at the instant when the pointer has zero velocity. Immediately on the fall of the chopper-bar B and C come into contact and the galvanometer is damped during the entire period occupied by its return to zero. The operations are then repeated, the usual period being one minute for each cycle.

§ 3. THEORY

There is little need to enter into the theory of the instrument here, as the treatment follows that found in the standard text-books on ballistic galvanometers. One point, however, is of interest, and that concerns the error in the record which is produced by an incorrect setting of the interval between the initiation of the ballistic throw and the fall of the chopper-bar. Once the throw has been started the displacement x of the pointer at any instant t is given by the expression

$$x = b \sin nt,$$

in which b is the maximum throw of the pointer, and $n = 2\pi/T$ where T is the period of one oscillation of the galvanometer.

Substitution in this expression of values of $\sin nt$ corresponding to errors of ± 5 per cent. in the timing, that is when $nt + 90^\circ = 45^\circ$, shows that the resultant error in the reading would be ± 0.31 per cent.

§ 4. APPLICATIONS

The principal application of the instrument at present seems to be for the recording of illuminations photoelectrically, and its great advantage over previous instruments is that the gain in sensitivity enables a vacuum cell to replace one with gas filling without having to be of large size. Since comparatively small illuminations are necessary, troublesome heating of the cathode is avoided. The vacuum cell has many well-known advantages over the gas-filled type; perhaps the most important is its constancy of sensitivity. The second advantage is that a steady accelerating-potential is unnecessary, since the cell is worked at saturation, so that mains supply may be used. The third advantage concerns particularly the method of recording which has been described. If a sufficiently high potential is applied to the cell, the current through it will be unaffected by the potential building up in the condenser, a convenient capacity for which is $2\mu F$. Each dot on the recorder, therefore, represents a true integration of the light which has fallen on the cell during the preceding minute.

In practice it is found that the arrangement shown in figure 1 is much less liable to be affected by leakage troubles than a straightforward circuit, provided that the condenser is placed near the cell. In other words, that part of the arrangement shown above the dotted line must be regarded as the light-sensitive unit. Three leads connect this unit to the recorder and battery, both of which may be removed to any distant position convenient for their housing.

The cells which have been used for this work are Osram type KV6, and no troubles have been experienced when the cell was kept reasonably dry. The condenser must of course be of good quality, although mica insulation is not necessary, and for this work a Ferranti type C2 has been used successfully. For some time a cell has been on a roof at Cambridge mounted in a water-tight metal box and exposed to daylight through a glass window incorporating a deep red screen. A typical

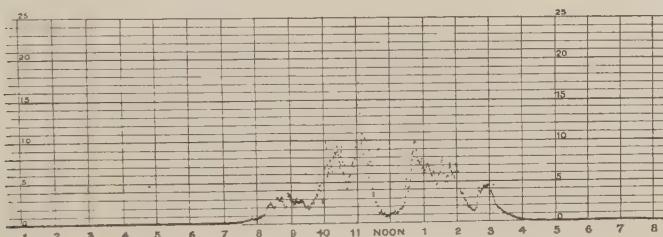


Fig. 3. Record of daylight through a red filter (Wratten No. 26).

record is reproduced in figure 3 and shows two points which are noteworthy: firstly the complete absence of any deflection during the period of darkness, and secondly the smoothness of the record resulting from the fact that the record is a succession of integrations over periods of one minute. There can be little doubt that the combination of a vacuum cell with the recorder described above gives records which are far more accurate than any that can be obtained with the aid of valve-amplifiers and other recording devices. Furthermore, the apparatus is so extremely simple.

Although the application of the recorder to the measurement of photoelectric currents has been described in detail it may be applied also to the recording of any d.c. leakage current where the voltage applied to the circuit is large compared to that reached by the condenser.

§ 5. ACKNOWLEDGMENT

Finally, my thanks are due to the Directors of the Cambridge Instrument Co., Ltd., for permission to publish this paper.

DISCUSSION

Mr R. W. WHIPPLE congratulated the author on the development of a piece of apparatus that might prove useful for the measurement of extremely small electric currents. It might eventually prove of service as a means of recording solar radiation by means of records from two or three photo-electric cells screened with glasses of varying spectral densities. Three or four different records obtained in this manner could be recorded on the same instrument.

Prof. A. O. RANKINE enquired what damping occurred during the throw of the galvanometer.

Mr A. F. DUFTON said that his experience suggested that the pointer would stick to the chopper bar unless these parts were cleaned.

The AUTHOR replied that the damping during the throw was negligible, and that if the bar were thoroughly cleaned a thread-recorder would work for 3 or 4 months without trouble due to sticking.

THE INSTRUMENTAL PHASE-DIFFERENCE OF SEISMOGRAPH RECORDS; AN ILLUSTRATION OF THE PROPERTIES OF DAMPED OSCILLATORY SYSTEMS

BY F. J. SCRASE, M.A., B.Sc., Kew Observatory

Received January 14, 1931. Read and discussed February 6, 1931.

ABSTRACT. A discussion is given of the method of interpretation of the maxima shown on the records of earthquakes during the surface-wave phase. The usual procedure is to treat the waves (which actually appear as beats) as being truly simple-harmonic and to apply the formulae which are derived on this assumption. It is shown that, in general, this procedure does not necessarily lead to the correct interpretation. In the case of direct registration the true earth-maximum may have occurred one half-period later than the time obtained by the usual correction. With galvanometric registration the maximum may have occurred either one, two, or three half-periods earlier than the time indicated by the usual formula due to Galitzin. Some curves are included to illustrate these points, and an attempt is made to obtain a mathematical explanation.

It is shown that there is no easy method of eliminating an ambiguity of one half-period. For direct registration, therefore, the phase-correction at present in use appears to be as good as the one alternative. In the case of galvanometric registration, although there are altogether four forms of phase-correction, the number of alternatives for any particular period cannot exceed two. The final recommendation in this case is that the correction suggested by Somville and which is one half-period less than Galitzin's, be adopted for general use.

§ I. INTRODUCTORY

THE data concerning important earthquakes published by seismological stations usually include some details of the prominent maxima which occur during the long or surface-wave phase. Most stations give times of maxima to the nearest second, and state whether the displacements are positive or negative. When mechanical or direct optical registration is employed one presumes that the times of maxima refer to actual earth-motion and that they include the usual correction for the phase-difference introduced by the pendulum: few stations explicitly state whether the corrections have been applied. With electromagnetic registration there enters a further complication, for there is great uncertainty as to what is the right phase-correction to apply. Various authors have attempted to settle the question once and for all, but differences in practice still remain; some stations use one form of correction, some use another, while at least two stations give the times of maxima as read directly from the records, and leave the reader to apply whichever correction he favours. These variations in practice lead to confusion, so this paper is written with the object of bringing the question to the light once more, and of reaching some conclusions which may lead to the adoption of a uniform procedure at all stations.

§ 2. MOTION OF PENDULUM FOR SIMPLE-HARMONIC
EARTH-MOTION

The motion of the pendulum under the influence of earth-movement may be represented by the usual equation:

$$\ddot{\theta} + 2e\dot{\theta} + n^2\theta + \frac{\ddot{x}}{l} = 0 \quad \dots\dots(1),$$

θ , x
 e , n , l
 T
 μ

where θ is the angular displacement of the pendulum, x the displacement of the earth, whilst e , n , and l are characteristic constants of the instrument. Actually $n = 2\pi/T$ where T is the free period of the pendulum. It is convenient to introduce another symbol μ for which

$$\mu^2 = 1 - e^2/n^2.$$

The solution of equation (1) when the earth-motion is simple-harmonic is quite straightforward. Thus, if

x_m	$x = x_m \sin(pt + d) \quad \dots\dots(2)$
p, t, d	then $\theta = Q \sin\{p(t - \tau) + d\} \quad \dots\dots(3)$
Q	where $Q = x/l(1 + u^2) \cdot \sqrt{1 - \mu^2 f(u)} \quad \dots\dots(4)$
τ	and $\tau = \frac{T_p}{2\pi} \cdot \tan^{-1} \left\{ \sqrt{(1 - \mu^2)} \cdot \frac{2u}{u^2 - 1} \right\} \quad \dots\dots(5)$

T_p, u, f

Here $T_p = 2\pi/p$, $u = T_p/T$ and $f(u) = \{2u(1 - u^2)\}^{1/2}$. If the pendulum is critically damped, $e = n$ and therefore $\mu^2 = 0$.

Equation (5) represents the phase-difference, expressed as time, between the motion of the pendulum and the motion of the earth. This time-lag τ is always positive and for critical damping it varies from zero, when u is infinitely large, to one half-period, when u is zero; when u is unity τ amounts to a quarter-period.

In view of what follows in this paper it is very important to draw attention here to the sign of θ . Suppose, for example, we are dealing with the vertical component and that, therefore, an earth-movement which is directed towards the zenith is regarded as being of positive sign. Then we must also regard the displacement θ of the pendulum as being positive if it is directed upwards. Equation (1) shows that for a sudden upward or positive impulse of the ground θ must be negative, i.e. the pendulum shows a displacement downwards. On the other hand, for sinusoidal earth-motion, if there is a positive maximum earth-displacement at a time t , then the corresponding maximum displacement of the pendulum τ seconds later than t is also positive. There is therefore a subtle distinction between the case of a sudden impulse and that of simple-harmonic motion, and it is thought that this distinction is not always realized or is sometimes neglected.

O. Somville* has drawn attention to the fact that, when the earth-motion is represented by equation (2), the differential equation (1) offers an alternative solution, which can be written as follows:

$$\theta = -Q \cos\{p(t - \tau') + d\} \quad \dots\dots(6),$$

τ'	$\tau' = \frac{T_p}{2\pi} \cdot \tan^{-1} \left\{ \frac{1}{\sqrt{1 - \mu^2}} \cdot \frac{1 - u^2}{2u} \right\} \quad \dots\dots(7)$
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* O. Somville, *Annales de l'Observatoire Royal de Belgique*, Brussels, 1918.

Since

$$\tan^{-1} \{ \sqrt{(1 - \mu^2)} \cdot 2u / (u^2 - 1) \} = \tan^{-1} \{ (1 - u^2) / 2u \sqrt{(1 - \mu^2)} \} + \pi/2.$$

Somville's expression only amounts to an alternative way of writing the usual solution.

He points out, in fact, that both solutions can be combined in a general expression.

$$\theta = Q \sin \{ p(t - \tau_m) + d + m\pi/2 \} \quad \dots\dots(8),$$

$$\tau_m = \tau + mT_p/4,$$

τ_m

m being a whole number, positive, zero, or negative. The ordinary formula corresponds to $m = 0$. When both earth-motion and recorded motion are continuous trains of simple-harmonic waves, it matters little which form of correction is applied, so long as due regard is given to signs.

§ 3. MOTION OF GALVANOMETER COIL FOR SIMPLE-HARMONIC EARTH-MOTION

For the complete theory of electromagnetic registration we are indebted to Galitzin*. The differential equation for the motion of the galvanometer coil is

$$\ddot{\phi} + 2n_1\dot{\phi} + n_1^2\phi + k\dot{\theta} = 0 \quad \dots\dots(9),$$

where ϕ is the angular displacement of the coil, θ the angular displacement of the pendulum, and n_1 , k are galvanometer constants. The constant n_1 is given by

$$n_1 = 2\pi/T_1,$$

where T_1 is the free period of the galvanometer, which is assumed to be critically damped. To arrive at a solution when the earth-motion is of the form

$$x = x_m \sin(pt + d),$$

Galitzin first obtains the formula (3), inserts this in equation (9) and finally obtains the following expression:

$$\phi = Q_1 \sin \{ p(t - \tau - \tau_1) + d \} \quad \dots\dots(10),$$

where $Q_1 = kx_m T_p / l \cdot 2\pi \cdot (1 + u_1^2) (1 + u^2) \sqrt{1 - \mu^2 f(u)}$ $\dots\dots(11)$,

and $\tau_1 = \frac{T_p}{2\pi} \cdot \left\{ \tan^{-1} \left(\frac{2u_1}{u_1^2 - 1} \right) + \frac{\pi}{2} \right\}$ $\dots\dots(12)$.

Here $u_1 = T_p/T_1$ and τ as before represents the phase-difference, expressed as time, between the pendulum-motion and the earth-motion, while τ_1 is the phase-difference between the galvanometer and the pendulum. We shall write $(\tau + \tau_1)$ as τ_2 .

In interpreting the galvanometer record, it is important not to have any misconception of the sign of the displacement. The galvanometer should be connected to the pendulum coils in such a way that the transmission coefficient k is positive. When the ground suffers a sudden impulse in a positive direction (upwards if we are considering the vertical component), the pendulum starts to move in a negative direction but the galvanometer records the impulse in the same direction as ground movement. If the earth-motion is simple-harmonic with a positive maximum at zero time, then the pendulum shows a positive maximum at a time τ , as we have already seen, and the galvanometer shows a positive maximum at a time τ_2 .

* Fürst B. Galitzin, *Vorlesungen über Seismometrie*, Teubner, Leipzig, 1914.

The paper by Somville is devoted mainly to putting forward evidence and arguments in favour of the adoption of an alternative formula for general use in determining the time of the earth-maximum from the time as given by a galvanometer record. A discussion of this alternative has been given by H. P. Berlage, Junr.* The formula may be written as follows:

$$\phi = -Q_1 \sin \{p(t - \tau - \tau_1') + d\} \quad \dots\dots(13),$$

 τ_1'

where

$$\tau_1' = \frac{T_p}{2\pi} \cdot \tan^{-1} \{(1 - u_1^2)/2u_1\} \quad \dots\dots(14).$$

This again is no more than an alternative way of writing the usual solution given by formulae (10), (11), and (12), for

$$\tan^{-1} \{(1 - u_1^2)/2u_1\} = \tan^{-1} \{2u_1/(u_1^2 - 1)\} - \frac{\pi}{2},$$

and the negative sign of equation (13) implies a further change of one half-period. The Galitzin correction refers to a recorded maximum which occurs with a lag given by τ_1 and is of the same sign as the earth-maximum. Somville's formula refers to a recorded maximum which occurs one half-period earlier than the Galitzin maximum and is of opposite sign to the earth-maximum. The evidence given in Somville's paper is regarded by him as being sufficiently conclusive for the complete rejection of the Galitzin formula. Unfortunately, however, he appears to ignore the reversal of sign which is implied by his formula. If the waves under consideration are truly simple-harmonic, then it is clear that both formulae are valid, provided that due regard is paid to the sign of the displacement. The two formulae, as Somville points out, can be combined into a general expression:

$$Q = -Q_1 \sin \{p(t - \tau - \tau_m') + d + m\pi/2\} \quad \dots\dots(15),$$

 τ_m'

where

$$\tau_m' = \frac{T_p}{2\pi} \left\{ \tan^{-1} \left(\frac{1 - u_1^2}{2u_1} \right) + \frac{m\pi}{2} \right\} \quad \dots\dots(16).$$

§ 4. GRAPHICAL SOLUTIONS FOR BEAT-WAVES

As a general rule the oscillations which occur during the surface-wave phase of an earthquake are not truly simple-harmonic. They appear to consist of a series of beat-waves which work up to a maximum amplitude soon after the commencement of the phase and then die down very gradually. The usual practice at observing-stations is to measure up the maximum amplitudes of a few of the well-marked beats. Since no convenient theoretical expression is available which will apply rigidly to the whole of the surface-wave phase and satisfactorily interpret both the beats and their waxing and waning, the usual procedure is to treat the oscillations as being simple-harmonic and to apply the theory which has been outlined in the foregoing sections for converting the recorded amplitudes and times into values which refer to the actual earth-motion. So far as the amplitudes are concerned, no appreciable errors are introduced, but it can be shown that this application of the simple theory to the case of beat-waves does not always give the correct answer for the time of the maximum amplitude in a beat.

* H. P. Berlage, Junr., *Seismische Registrirungen in De Bilt*, No. 9. (Koninklijk Nederlandsch Meteorologisch Institut, 1921.)

A slightly more rigid interpretation of the records can be obtained if the earth-motion is regarded as being produced by the interference of two trains of simple-harmonic waves of slightly different periods, thus:

$$x = a \cos(pt + d) + b \cos(p't + d').$$

p, d, p', d'

Now we can deduce the recorded motion by treating each of the component waves separately, applying the formulae for simple-harmonic waves and summing the motions so obtained. In the case of the pendulum for instance:

$$\theta = A \cos\{p(t - \tau) + d\} + B \cos\{p'(t - \tau') + d'\},$$

A, B

where A and B involve the appropriate magnification factors while τ and τ' are the corresponding instrumental phase-differences, given by equation (5). The case of the galvanometer is quite similar but the magnifications will be different and the instrumental phase-differences will be $(\tau + \tau_1)$ and $(\tau' + \tau_1')$, given by equations (5) and (12).

The effect of this treatment is most readily seen by consideration of some numerical examples. In each of the figures accompanying this paper there are two curves, one representing the earth-motion, the other showing recorded motion. The curves are obtained in the manner indicated above and are drawn to scale as accurately as possible. The instruments are assumed to be critically damped and to have free periods of 25 seconds. In general it is not difficult to pick out the maximum displacement in each group of waves; if there is any doubt the numerical values will of course settle which peak is the largest. As would be expected, the instrumental phase-differences cause some change of character in the motion; for example, if the original motion is symmetrical about the maximum of a beat, the recorded motion is not necessarily so. On account of this, it cannot strictly be said that any particular point on the recorded-motion curve corresponds with some particular point in the original motion. The best we can do is to admit a correspondence between the maximum displacements for earth-motion and recorded motion in each beat; that, at any rate, interests us from the practical point of view. What we want to discover, therefore, is how far the time-differences between the corresponding maxima fit in with the differences which are obtained by the ordinary formulae for simple-harmonic waves.

§ 5. GRAPHICAL SOLUTIONS; MOTION OF PENDULUM

In figure 1 the earth-motion is assumed to be

$$x = \cos(2\pi t/36) + \cos(2\pi t/44).$$

The greatest displacement in the beat is therefore a positive one at zero time, and the quasi-period T_p of the resultant oscillations is 40 sec. Since the free period T of the pendulum is 25 sec., u , which is T_p/T , is 1.6. The appropriate relative magnification factors and phase-differences give for the pendulum-motion:

$$\theta = 319 \cos\{2\pi(t - 6.9)/36\} + 239 \cos\{2\pi(t - 7.1)/44\}.$$

It will be seen from the curve that the greatest pendulum displacement P is of the same sign as the earth-maximum, and occurs 7 sec. later. Now this is the phase-

difference τ (equation 5) for simple-harmonic waves of 40-sec. period. The application of the usual formula therefore gives the correct answer in this particular case.

The earth-motion represented in figure 2 is the sum of the two cosine waves of periods 4·5 and 5·5 sec. respectively and, since no initial phase-difference is assumed, the greatest maximum is at zero time. The quasi-period of the resultant is 5 sec. and u is 0·2. The pendulum-motion is given by:

$$\theta = 96 \cos \{2\pi(t - 2\cdot0)/4\cdot5\} + 94 \cos \{2\pi(t - 2\cdot4)/5\cdot5\}.$$

In this case the greatest pendulum displacement Q is a negative one and is 0·3 sec. in advance of the earth-maximum. The usual formula indicates a lag of 2·2 sec. If, therefore, we were interpreting the recorded motion, we should measure the time of the maximum Q and say that the earth-maximum occurred 2·2 sec. earlier. This

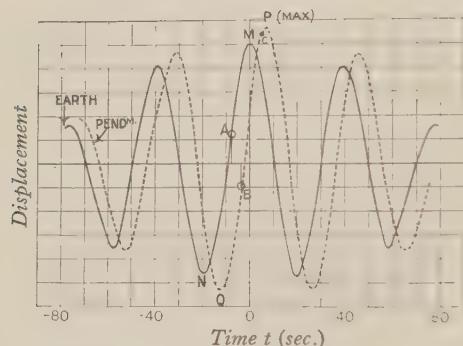


Fig. 1. Earth-motion and pendulum-motion; $T=25$ sec., $T_p=36$ sec., $T_{p'}=44$ sec., $d=0$ sec.

Fig. 2. Earth-motion and pendulum-motion; $T=25$ sec., $T_p=4\cdot5$ sec., $T_{p'}=5\cdot5$ sec., $d=0$ sec.

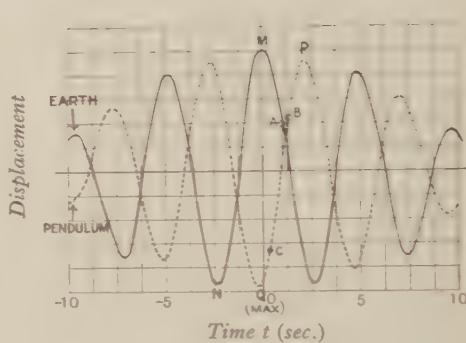
would indicate the peak N as being the greatest earth-maximum. Obviously this procedure is faulty. The correct procedure in this particular case is to apply a time-correction given by $(\tau - \frac{1}{2}T_p)$, which in this case is $-0\cdot3$ sec., and to reverse the sign. This corresponds to the case where $m = (-2)$ in the general formula suggested by Somville. Therefore when we turn from simple-harmonic waves to beat-waves, the difference between the alternative formula becomes significant. Some attempt will be made later to discover when it is better to use one formula and when the other.

§ 6. GRAPHICAL SOLUTIONS: MOTION OF GALVANOMETER COIL

In figure 3 the earth-motion is the same as for figure 1. The motion of the galvanometer coil is given by:

$$\phi = 174 \cos \{2\pi(t - 22\cdot8)/36\} + 123 \cos \{2\pi(t - 25\cdot1)/44\}.$$

The recorded-maximum S is of opposite sign to the earth-maximum M and has a retardation of 4 sec. The Galitzin formula for an oscillation of 40-sec. period



$(u = 1.6)$ gives a retardation of 24 sec. Using this formula we should interpret S as corresponding to the earth-maximum N . This particular case fits in with the Somville formula (14) or with $m = 0$ in his general formula (15); we should therefore apply a time-correction of $(\tau_2 - \frac{1}{2}T_p)$ sec. and reverse the sign.

The earth-motion in figure 4 has a quasi-period of 5 sec. ($u = 0.2$) and the recorded curve is given by

$$\phi = 198 \cos \{2\pi(t - 5.1)/4.5\} + 238 \cos \{2\pi(t - 6.1)/5.5\}.$$

The greatest recorded maximum T is of the same sign as the earth-maximum M and has a retardation of 0.6 sec. Using the Galitzin formula, which gives a lag of 5.6 sec., we should expect the earth-maximum to be at O , whereas using Somville's formula, which gives a retardation of 3.1 sec., we should expect the maximum to be at N . It will be seen that the appropriate correction to be made is $(\tau_2 - T_p)$ sec. and that there is no reversal of sign. This corresponds to $m = (-2)$ in the general formula (15).

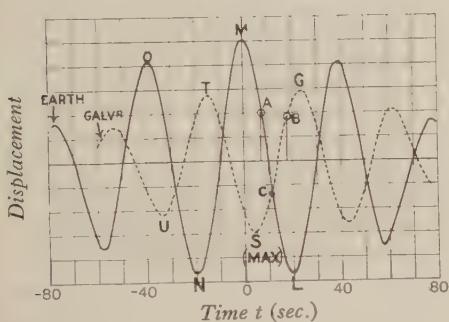


Fig. 3. Earth-motion and galvanometer-motion; $T = T_1 = 25$ sec., $T_p = 36$ sec., $T_{p'} = 44$ sec., $d = 0$ sec.

Fig. 4. Earth-motion and galvanometer-motion; $T = T_1 = 25$ sec., $T_p = 4.5$ sec., $T_{p'} = 5.5$ sec., $d = 0$ sec.

In figure 5 an initial phase-difference has been introduced into the earth-motion, which is given by:

$$x = \cos \{2\pi(t - 1)/36\} + \cos \{2\pi t/44\}.$$

The curve for the galvanometer coil is given by:

$$\phi = 174 \cos \{2\pi(t - 1 - 22.8)/36\} + 123 \cos \{2\pi(t - 25.1)/44\}.$$

The earth-maximum M occurs at 0.5 sec. and the recorded maximum G is 24 sec. later. This case corresponds exactly to the Galitzin formula, which gives a retardation of 24 sec. for $u = 1.6$. Obviously the Somville formula would lead to an incorrect interpretation by indicating L as the earth-maximum.

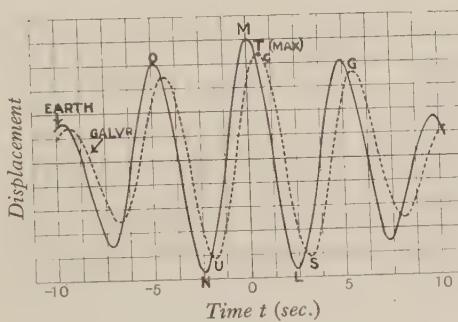
The earth-motion in figure 6 is represented by

$$x = \cos \{2\pi(t + 0.1)/2.25\} + \cos \{2\pi t/2.25\},$$

while the motion of the galvanometer coil is:

$$\phi = 216 \cos \{2\pi(t + 0.1 - 2.65)/2.25\} + 257 \cos \{2\pi(t - 3.20)/2.75\}.$$

The earth-maximum M occurs at -0.05 sec., while the galvanometer-maximum U ,



which is of opposite sign, is 0.85 sec. in advance of M . In this case the Galitzin correction τ_2 , which for $u - 0.1$ is 2.9 sec., would indicate the peak P on the earth curve as being the maximum. The Somville correction, which is one half-period less than the Galitzin correction, i.e. 1.65 sec., would indicate the peak O . Both, therefore, lead to incorrect interpretations, and the suitable correction for this particular case is three half-periods less than the Galitzin correction, i.e. $(\tau_2 - 1\frac{1}{2}T_p)$. A reversal of sign must be made. The corresponding value of m in Somville's general formula is -4.

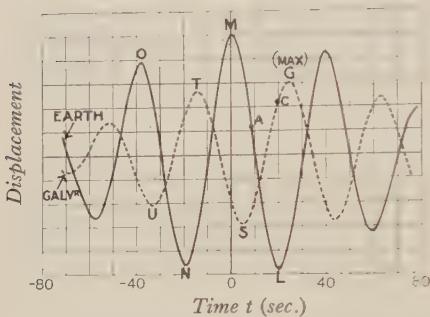


Fig. 5. Earth-motion and galvanometer-motion; $T = T_1 = 25$ sec., $T_p = 36$ sec., $T_{p'} = 44$ sec., $d = 1$ sec.

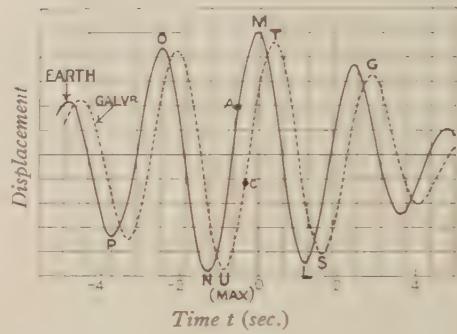


Fig. 6. Earth-motion and galvanometer-motion; $T = T_1 = 25$ sec., $T_p = 2.25$ sec., $T_{p'} = 2.75$ sec., $d = 0.1$ sec.

It is seen then that there are at least four different forms of phase-correction which may apply to the case of beat-waves. Can we formulate some rules as to when each form is applicable?

§ 7. MATHEMATICAL ANALYSIS OF PENDULUM MOTION

The mathematical interpretation of the results which we have obtained graphically can be made more clear if, at first, we restrict ourselves to the simple case in which the two trains of simple-harmonic waves forming the beats have no initial phase-difference. Suppose then that the earth-motion is represented by:

$$\delta p = a \cos \{(p + \delta p)t\} + b \cos \{(p - \delta p)t\}.$$

This can also be written in the following form:

$$x = \sqrt{(a^2 + b^2 + 2ab \cos 2\delta p t)} \cdot \cos \left(\frac{1}{2}pt + \tan^{-1} \left(\frac{a - b}{a + b} \tan \delta p t \right) \right) \dots \dots (17).$$

The resultant can be regarded as approximately a simple-harmonic motion whose quasi-frequency p is the arithmetic mean of the component frequencies and whose amplitude alternates between the sum of and the difference between the component amplitudes, the variation having a frequency, $2\delta p$, equal to the difference between the component frequencies. If both the difference between the frequencies and the difference between the amplitudes are small, the variable phase-difference will be very small for oscillations near the middle of a beat and we can neglect it. The beat,

represented by the first member of the product (17), is a maximum at zero time, and therefore coincides with one of the maxima given by the second member, thus making this maximum the largest in a beat. This, of course, we expect, because there is no initial phase-difference.

Now the motion of the pendulum is given by:

$$\theta = A \cos [(p + \delta p) \{t - (\tau + \delta\tau)\}] + B \cos [(p - \delta p) \{t - (\tau - \delta\tau)\}] \dots (18),$$

where A and B are obtained from formula (4), while $(\tau + \delta\tau)$ and $(\tau - \delta\tau)$ are the phase-differences given by formula (5). We wish to find the time of the largest amplitude in the beat. It is best to express θ as a product:

$$\theta = \sqrt{A^2 + B^2 + 2AB \cos 2\{\delta p \cdot t - \overline{\delta p \cdot \tau + p \cdot \delta\tau}\}}$$

$$\cos \left[pt - \overline{p\tau + \delta p \cdot \delta\tau} + \tan^{-1} \left\{ \frac{A - B}{A + B} \tan (\delta p \cdot t - \overline{\delta p \cdot \tau + p \cdot \delta\tau}) \right\} \right] \dots (19).$$

Here again, under the conditions specified, we can neglect the variable phase-difference introduced by the inverse tangent term. It should be noted, however, that this phase-difference differs by a fixed amount $(\delta p \cdot t + p \cdot \delta\tau)$, from that of the original oscillations. The term $\delta p \cdot \delta\tau$ is small enough to be left out of consideration. We are left with:

$$\theta = \sqrt{A^2 + B^2 + 2AB \cos 2\{\delta p \cdot t - (\delta p \cdot \tau + p \cdot \delta\tau)\}} \cos p(t - \tau) \dots (20).$$

The second member of this product represents the oscillations of mean frequency p (mean period T_p) and they have a phase-difference τ which is given by the usual equation (5) for simple-harmonic waves of period T_p . The first member of the product will tell us which of the oscillations has the largest amplitude. Thus the beats themselves reach a maximum when

$$t = \tau_b = \tau + p\delta\tau/\delta p = \tau - T_p\delta\tau/\delta T_p \dots (21),$$

and this is the phase-difference, expressed as time, of the beats of frequency δp . It can be seen that the question which is the greatest maximum in a beat rests on the value of $\delta\tau/\delta T_p$. If this is zero, then the maximum which has a retardation given by τ is the greatest; in other words, the application of the ordinary formula for simple-harmonic waves gives the correct interpretation. If, however, $\delta\tau/\delta T_p$ is sufficiently large the beats themselves may be retarded (or advanced) by an amount so different from the retardation τ of the oscillations, that an earlier or later maximum (positive or negative) than that given by the usual formula may become the largest in a beat.

If the formula (5) for τ is plotted against T_p , it becomes obvious that there are an infinite number of pairs of periods which give the same value for $\delta\tau/\delta T_p$. So long as we restrict ourselves to pairs which have not large differences, these pairs will, to a good approximation, all have the same mean, and the corresponding value of $\delta\tau/\delta T_p$ will be the value of the differential coefficient $d\tau/dT_p$ when T_p is the mean period of the component waves. If $d\tau/dT_p$ is, say, $\frac{1}{4}$ when T_p is 20 sec., then $\delta\tau/\delta T_p$ will also be $\frac{1}{4}$ for pairs of periods given by $(T_p + n)$ and $(T_p - n)$ so long as n is not

too large. The differential coefficient of τ is easily obtained. For simplicity let us assume that the pendulum is critically damped. Then equation (5) becomes

$$\tau = (T_p/2\pi) \tan^{-1} \{2u/(u^2 - 1)\}.$$

This can be written:

$$\tau = (T_p/2\pi) (\pi - 2 \tan^{-1} u).$$

Therefore we have

$$\begin{aligned} d\tau/dT_p &= \frac{1}{2} - \pi^{-1} \tan^{-1} u - u/\pi(1+u^2), \\ &= \tau/T_p - u/\pi(1+u^2). \end{aligned}$$

The lag of the beats is then (from 21)

$$\tau_b = T_p \cdot u/\pi(1+u^2).$$

When there is no initial phase-difference in the original components $T, d\tau/dT_p$ is the time by which the beat maximum is in advance of the particular maximum that falls at time τ . If it is less than one quarter-period, then the maximum at τ will be the greatest in the beat. If it is greater than a quarter-period, then the negative maximum at $(\tau - \frac{1}{2}T_p)$ will be the maximum maximorum. The two will have equal amplitudes when $T_p d\tau/dT_p$ is exactly one quarter-period. This occurs when:

$$\frac{1}{4} = \frac{1}{2} - \pi^{-1} \tan^{-1} u - u/\pi(1+u^2).$$

Writing $\tan^{-1} u = \psi$, we find that

$$\pi/4 = \psi + \sin \psi,$$

whence

$$\psi = 22^\circ 8,$$

and

$$u = 0.421.$$

Table 1 gives some other values of the phase-differences of the oscillations and of the beats expressed as fractions of the mean period T_p of the oscillations. All of the values are positive: i.e. they are retardations. This table affords an explanation of the differences found by the graphical method. With reference to figure 1 for

Table 1.

u	τ/T_p	$d\tau/dT_p$	τ_b/T_p
0	0.50	0.50	0
0.2	0.44	0.48	0.06
0.3	0.41	0.32	0.09
0.42	0.37	0.25	0.12
1.0	0.25	0.09	0.16
1.6	0.17	0.03	0.14
∞	0	0	0

which u is 1.6, the point C on the pendulum curve is marked as being the time of the maximum of the beat given by τ_b . In this case it is $0.03T_p$, i.e. 1.2 sec. in advance of P . P therefore is the greatest oscillation. In figure 2, on the other hand, the point C corresponding to maximum of the beat is $0.48T_p$, i.e. 2.4 sec. in advance of P or $0.06T_p$, i.e. 0.3 sec. behind the corresponding earth-maximum at zero time. It is clear then that the peak Q will have the greatest amplitude. Remembering that we are at present confined to the case in which there is no initial phase-

difference between the original cosine components, we can say that so long as $d\tau/dT_p < 0.25$, i.e. when $u > 0.42$, the greatest recorded maximum of the beat will be that indicated by the usual formula for τ . If $d\tau/dT_p > 0.25$, i.e. if $u < 0.42$, then the greatest maximum is recorded one half-period earlier and is of opposite sign to the earth-maximum. When $u = 0.42$ the beat-maximum falls half-way between the peaks P and Q , which then have equal amplitudes.

Unfortunately the rule breaks down when an initial phase-difference between the two earth components is introduced. The effect is that the maximum of the earth beat no longer coincides with a maximum of an oscillation. It seems unnecessary to work through the theoretical expressions again, for they are simply an extension of those already given but with added fixed phase-differences. It suffices to state that, whatever the initial phase-differences, the retardation of the oscillations is still given by the usual formula for τ and the retardation of the beats themselves behind those of the earth-motion is still given by the τ_b , equation (21). We can no longer say, however, that the beat-maximum is in advance of the oscillation by $T_p d\tau/dT_p$. If the initial phase-difference is such that the beat-maximum of the earth occurs at a time $= rT_p$ in advance or in retard of the maximum oscillation, then on the record the beat-maximum will occur at a time $T_p (d\tau/dT_p \pm r)$ from the maximum oscillation that is indicated by the usual formula τ . Thus in figure 1 we might have chosen an initial phase-difference such that the maximum of the beat-motion (i.e. the wave of frequency $2\pi/(\frac{1}{2}(44 - 36))$) occurred at a time given by the point A . The peak M would still have the maximum amplitude. Since, however, the beats themselves are retarded by $0.06 T_p$, the corresponding point on the pendulum curve is given by B . Although $u > 0.44$ the peak Q would have the maximum recorded amplitude. Similar reasoning can be applied to figure 2 to show that the maximum amplitude may occur at a time which conforms to the ordinary formula. It appears therefore that we cannot decide, from a knowledge of the mean period T_p alone, which correction, τ or $(\tau - \frac{1}{2}T_p)$, is applicable. We must have some information concerning the phase-difference between the original components. Unfortunately this is not easily obtained from the records; the work involved is far too troublesome for routine procedure. The best course we can adopt is to use one correction throughout, always bearing in mind the fact that the maximum earth-oscillation of opposite sign which occurs one half-period earlier or later, according to whether we use τ or $(\tau - \frac{1}{2}T_p)$, may be slightly greater than that which occurs at the time indicated by the correction.

It should be pointed out that in the case of direct registration there can be only two alternative corrections. All cases of initial phase-difference are covered by the limits $\pm \frac{1}{4}T_p$ for the time between the beat-maximum and the largest oscillation of the earth-motion. The corresponding time-difference on the pendulum curve therefore must lie between $T_p (d\tau/dT_p + \frac{1}{4})$ and $T_p (d\tau/dT_p - \frac{1}{4})$. From table 1 it can be seen that so long as the oscillations are of finite period this time-difference must be less than $+\frac{3}{4}T_p$, and greater than $-\frac{1}{4}T_p$. It is only when the periods become infinitely small or infinitely long that two further alternatives may theoretically be possible and these cases are of no practical interest.

§ 8. MATHEMATICAL ANALYSIS OF MOTION OF GALVANOMETER COIL

The method of reasoning which we have used for the case of pendulum-motion applies equally well to the case of the galvanometer coil. All we have to do is to substitute τ_2 for τ . The oscillations forming the beats are retarded by a time τ_2 , and the beats themselves are retarded by

$$(\tau_2 - T_p \cdot \delta\tau_2/\delta T_p),$$

no matter what the initial phase-difference. If, for simplicity, we assume that the free periods of the galvanometer and the pendulum are equal and that both instruments are critically damped, then we may write:

$$\begin{aligned}\tau_2 &= \frac{T_p}{2\pi} \left\{ 2 \tan^{-1} \left(\frac{2u}{u^2 - 1} \right) + \frac{\pi}{2} \right\} \\ &= \frac{T_p}{2\pi} (2.5\pi - 4 \tan^{-1} u);\end{aligned}$$

whence

$$\begin{aligned}d\tau_2/dT_p &= 1.25 - 2\pi^{-1} \tan^{-1} u - 2u/\pi (1 + u^2) \\ &= \tau_2/T_p - 2u/\pi (1 + u^2).\end{aligned}$$

The lag τ_b of the beats is then given by:

$$\tau_b = 2u \cdot T_p/\pi (1 + u^2),$$

which is double the lag that we found for the case of the pendulum. When there is no initial phase-difference between the original components, $T_p \cdot d\tau_2/dT_p$ is the time by which the recorded beat-maximum is in advance of the oscillation at τ_2 . If it is zero, the beat-maximum coincides with the oscillation at τ_2 , making it the greatest in the beat. If $T_p \cdot d\tau_2/dT_p$ is one half-period, the beat-maximum coincides with the earlier negative peak at $(\tau_2 - \frac{1}{2}T_p)$. This occurs when:

$$d\tau_2/dT_p = \frac{1}{2} = \frac{5}{4} - 2\pi^{-1} \tan^{-1} u - 2u/\pi (1 + u^2),$$

or, writing $\tan^{-1} u = \psi$, $\frac{3}{4}\pi = 2\psi + \sin \psi$,

$$\psi = 39^\circ 9 \quad \text{or} \quad u = 0.836.$$

If $T_p \cdot d\tau_2/dT_p$ is one whole period the beat-maximum coincides with the positive peak at $(\tau_2 - T_p)$. This occurs when:

$$\pi/4 = 2\psi + \sin 2\psi,$$

i.e. when

$$\psi = 11^\circ 4 \quad \text{or} \quad u = 0.202.$$

The following other numerical values will help to explain the results already obtained graphically.

Table 2.

u	τ_2/T_p	$d\tau_2/dT_p$	τ_b/T_p
0	1.25	1.25	0
0.1	1.17	1.12	0.06
0.20	1.12	1.00	0.12
0.44	0.98	0.75	0.23
0.84	0.80	0.50	0.30
1.60	0.60	0.32	0.28
∞	0.25	0.25	0

In all of the curves showing galvanometer-motion the peak marked G is that which corresponds with the lag τ_2 behind the earth-maximum M (τ_2 being the Galitzin correction). In figure 3 the earth components have no initial phase-difference, so that the beat-maximum coincides with M and the corresponding beat-maximum C on the galvanometer curve is delayed by $0.28T_p$, or it is in advance of G by $0.32T_p$. The peak S therefore has the greatest amplitude, and the proper correction to apply is $(\tau_2 - \frac{1}{2}T_p)$, as suggested by Somville. A reversal of sign must, however, be given. A similar reasoning applied to figure 4 shows that the recorded beat-maximum C comes exactly one whole period in advance of G , making T the largest oscillation. In this case neither the Galitzin nor the Somville corrections apply, but a lag given by $(\tau_2 - T_p)$.

In figure 5 the initial phase-difference causes the beat-maximum of the earth-motion to occur at a time $0.2T_p$ after M , i.e. at the point A . Table 2 shows us that there is a further delay of $0.28T_p$ with the galvanometer, and this gives us the beat-maximum at C . The peak G is this time the maximum, and so the Galitzin formula is applicable. It should be noted that figure 3, for which T_p is the same, would also yield this information, the points marked A and B being chosen so that the time between them is $0.28T_p$.

In figure 6 the retardation of the beats is $0.06T_p$, and A and C correspond to the times of the beat-maxima. The oscillation of largest amplitude is the peak U . The appropriate correction therefore is $(\tau_2 - 1\frac{1}{2}T_p)$, which in this case means an advance, and the sign must be reversed.

As in the case of the pendulum, there is no means of deciding which is the proper correction to apply unless the initial phase-difference is known. It can be shown, however, that for any particular case the number of alternatives can be narrowed down to two. All cases of initial phase-difference can, as before, be covered by superimposing $\pm \frac{1}{4}T_p$ on the difference between the retardation of the oscillations and that of the beats. There is therefore an ambiguity which cannot be greater than $+\frac{1}{4}$ or less than $-\frac{1}{4}$ in the values of $d\tau_2/dT_p$. If then $d\tau_2/dT_p < 1.25$ and > 0.5 , the Galitzin correction can never apply, for the recorded beat-maximum must be more than a quarter of a period in advance of the maximum oscillation given by τ_2 . If $d\tau_2/dT_p > 1.0$, neither the Galitzin nor the Somville corrections can apply. On the other hand, the correction $(\tau_2 - 1\frac{1}{2}T_p)$ does not fit if $d\tau_2/dT_p < 1.0$, neither does the correction $(\tau_2 - T_p)$ if $d\tau_2/dT_p < 0.5$. This information is summarized thus:

Limits of u	Alternative corrections
$\infty > u > 0.84$	$\tau_2 ; (\tau_2 - \frac{1}{2}T_p)$
$0.84 > u > 0.2$	$(\tau_2 - T_p); (\tau_2 - \frac{1}{2}T_p)$
$0.2 > u > 0$	$(\tau_2 - T_p); (\tau_2 - 1\frac{1}{2}T_p)$

Those corrections which differ from τ_2 by an odd half-period imply a reversal of sign. Table 3 gives some numerical values for a case in which the instrumental period is 20 sec.

Table 3.

$\frac{T_p}{T} = u$	Earth period T_p	Retardation of registered maximum			
		Maximum of same sign as that of earth-movement		Maximum of opposite sign	
		True	Galitzin	True	Somerville
	sec.	sec.	sec.	sec.	sec.
1.5	30	18.8	18.8	3.8	3.8
1.0	20	15.0	15.0	5.0	5.0
0.6	12	— 1.1	10.9	4.9	4.9
0.4	8	0.0	8.0	4.0	4.0
0.15	3	0.5	3.5	— 1.0	2.0

§ 9. CONCLUSIONS

Let us now reconsider how best we can interpret a record of the principal phase of an earthquake. We have on the record a group of waves of period T_p , which form a beat. In general the amplitude of one oscillation on the record will be greater than the amplitudes of neighbouring oscillations in the beat. This displacement is measured and is converted into actual earth-movement by applying the magnification-factor for sinusoidal waves. This procedure is sufficiently accurate for all practical purposes so long as the beats are reasonably long, but it is not strictly correct on account of the change in character of the beat-motion from the original form. The time, on the record, of the maximum displacement in the beat is measured and the next step is to arrive at the time of the corresponding oscillation in the earth-motion. For routine measurements it is scarcely worth while endeavouring to arrive at the initial phase-difference between the waves into which the beats could be resolved, and without this knowledge it is impossible to decide what shall be taken as the corresponding oscillation in the earth-motion.

In the case of direct registration, we can definitely say that the largest earth-displacement of the same sign as the recorded displacement occurred at a time τ in advance of the recorded time (τ being given by the usual formula). It must be remembered, however, that the oscillation of opposite sign which occurred at a time $(\tau - \frac{1}{2}T_p)$ in advance of the recorded time may have been greater. We can, at any rate, definitely conclude that no advantage will be obtained by changing from the present procedure of using the ordinary formula, equation (5), and adopting instead a correction which is one half-period less and which carries a reversal of sign. Whichever formula is adopted, it is very important that the distinction between the signs of the displacements in the case of a sudden impulse and in the case of sinusoidal motion be fully appreciated; as was pointed out in § 2, a sudden impulse is recorded with a reversal of sign.

It is not easy to decide the best course to adopt in the case of galvanometric registration. If we make the convention of always giving the time of the largest earth-displacement which has the same sign as the recorded maximum, then we must

apply Galitzin's correction τ_2 if $u > 0.84$, but when $u < 0.84$ we must reduce the Galitzin correction by one whole period. This is definitely better than retaining the Galitzin formula for all periods since that formula cannot apply when $u < 0.84$, but to have two formulae in use may lead to confusion. There is a practical consideration which indicates that a better course is to adopt the Somville formula ($\tau_2 - \frac{1}{2}T_p$). It has been shown that the range over which this formula cannot apply is that between $u = 0$ and $u = 0.2$. Now most instruments are tuned to periods not exceeding 25 sec. This means that all earth-waves of periods greater than 5 sec. correspond to values of u in excess of 0.2. Since, during the surface-wave phase, the periods rarely, if ever, fall as low as 5 sec., there is no reason why the Somville formula should not give the correct result in as many cases as if the two alternatives were used. It is finally recommended, therefore, that for time-measurements of the maxima occurring in the principal phases of earthquakes the Somville formula be adopted as a phase-difference correction. The reversal of sign which this formula implies must, of course, be remembered. A reservation must be made if phase-difference corrections are to be applied to waves of such short periods as often occur in the case of microseisms.

§ 10. ACKNOWLEDGMENT

In conclusion I wish to thank Dr F. J. W. Whipple, Superintendent of Kew Observatory, for suggesting this investigation in the first place and also for helpful criticism.

DISCUSSION

Sir A. S. EDDINGTON. The simple-harmonic solution represents a steady state, established from the beginning of time, with the pendulum and the ground oscillating in such a phase that they do not upset the steady condition. In that case there is no meaning in trying to pick out a single crest on the ground-wave as particularly responsible for a given crest on the pendulum-wave. (The strong damping would, however, make it far-fetched to associate crests too wide apart in time). The problem thus arises only if there is some variation from steady simple-harmonic motion—beats or a sudden pulse—so that the appropriate formula for correlating points on the two curves is necessarily the one given by Mr Scrase for the case of beats. If I have understood rightly, that is the essential point that his paper develops.

MR T. SMITH suggested that the identification of a particular crest with the disturbance was as arbitrary with a simple group of waves as with a simple-harmonic system. The association seemed to him to be essentially a matter of convention, and the criterion to be applied in judging between different conventions might well rest on practical experience of the convenience of different choices rather than on mathematical grounds alone. Thus with certain methods of computing tides it had been found convenient to associate component tides with the meridional passage of the sun or moon which took place about a day and a half before the tide rather than with another crossing which might equally well have been chosen.

AUTHOR's reply. Sir Arthur Eddington has summed up the essential points of the problem very clearly. The general solutions for a steady state of simple-harmonic motion show that one cannot regard any particular peak on the record as being produced by a given peak in the earth-motion. But when some irregularity is superimposed on the simple-harmonic motion, it is possible to interpret a corresponding irregularity on the record and to obtain a particular case of the general formula which will apply.

Mr Smith has remarked that since group-velocities are in question the problem remains indeterminate. I gather that he refers to the lag of the waves relative to that of the beats. It is true that this changes the form of the beats to some extent, but for practical purposes it is appropriate to consider the maximum displacement in the recorded beat as corresponding to the maximum displacement in the original beat. This procedure does not give an ambiguous result unless the positive and negative displacements in the middle of a beat are equal.

NOTE ON THE ELIMINATION OF THE β WAVE-LENGTH FROM THE CHARACTERISTIC RADIATION OF IRON

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*Communicated by Dr G. W. C. Kaye, January 1, 1931. Read and discussed
February 20, 1931.*

ABSTRACT. A practical method of eliminating the β wave-length from the characteristic K-radiation of iron is described. The method is based upon the selective absorption produced by a thin film of pure manganese which is obtained in the required form by electrodeposition upon aluminium foil.

§ 1. INTRODUCTION

THE characteristic K-radiation direct from an iron anticathode is very commonly used in X-ray analysis. The spectrum of an irradiated substance is complicated, however, by the presence of reflections due to wave-lengths other than the K_α component. The main difficulties arise from the K_β wave-length. In the case of substances of high crystal-symmetry, which give comparatively few lines, or of those obtainable in the form of single crystals, the lines from the different faces of which need not be superimposed, the extra spectra due to the β component can be readily recognized and allowance can be made for them. But in the majority of cases, especially if the power method of analysis be used, difficulty is experienced in determining definitely whether certain lines should be assigned to the α or to the β wave-lengths. In consequence, the elimination of the latter component from the radiation incident on a substance under examination is often very desirable. The object of the present paper is to describe a simple method of accomplishing this by the method of selective absorption. The removal of undesired wave-lengths could, of course, be secured once and for all by the use of a beam which had been rendered monochromatic by preliminary reflection from a standard crystal face. The disadvantage of this method lies in the considerable decrease in intensity which would follow upon a double reflection. Moreover, the efficacy with which a screen of nickel foil, in the analogous case of copper, removes the copper K_β wave-length by preferential absorption, would suggest that the extreme method of primary reflection is not necessary.

The appropriate absorbing material to be employed in the case of iron is manganese, since the wave-length of the absorption edge has a value less than that of the α and greater than that of the β wave-length. The discontinuity in the absorption/wave-length curve for manganese occurs, therefore, at a value which involves a much greater absorption of the iron β than of the α wave-length. It is desirable

that the screen should not reduce the intensity of the α component any more than is necessary. On that account, the use of screens made up of manganese compounds, such as the dioxide, is, as most workers will have found, inefficient in practice because of the additional absorption of the beam caused by the presence of the other constituents of the molecule. So far as the author is aware, the idea of using a thin film of manganese prepared for this purpose by electrodeposition is new, and, as the matter is of some practical importance to X-ray workers, it was considered worth while to outline the method.

§ 2. EXPERIMENTAL DETAILS

The films of manganese were first deposited on aluminium foil. Such foil can be obtained so thin that the absorption of radiation becomes very small. Also the presence of the aluminium backing has the advantageous effect of increasing the contrast of the lines on an X-ray photograph by absorbing most of the softer rays which would otherwise add to the continuous background. In consequence it was found that the use of the screen need increase the time of exposure by very little. If required, however, the manganese film can be fastened to a base of cellophane or some such material and the aluminium dissolved away. Alternatively, if an X-ray tube of the experimental demountable type be employed, the film may replace the usual aluminium window. It was found, too, that the thicker films could be stripped from the aluminium.

The arrangement of the electrolytic bath was as follows*. The anode consisted of a piece of platinum foil which was suspended in a strong solution of ammonium sulphate. This solution was separated from the rest of the bath by a porous pot. The catholyte contained per litre 250 gm. of pure manganese sulphate crystals and 100 gm. of ammonium sulphate. The cathode was a piece of thin aluminium foil which was smoothed out upon and attached by adhesive to a piece of glass. A very smooth surface appeared to be required in view of the weak throwing-power of the manganese ion. A preliminary cleaning of the surface by benzene and dilute acid was made. A certain amount of trouble was encountered in securing a deposit composed of crystal grains fine enough to give a smooth continuous surface. The manganese tended to deposit first as a fine layer with a metallic lustre, and then to increase further in thickness by growing large crystals. It was found, however, that the grain size varied critically with the current density and the temperature of the bath, and these could be adjusted to suit the type of deposit required. A current-density rather larger than usual, namely about 250 ma. cm.², with the electrolyte at 35° C. gave good results with the bath described, and a film sufficiently thick and uniform to produce an effective screen could be obtained after the current had been passed for about one hour. If the time of deposition was prolonged too far, the weakening of the bath appeared to have the effect of increasing again the grain-size of the layer. After being washed and dried with alcohol, the film was covered with a little varnish to prevent undue oxidation.

* A. J. Allmand and A. N. Campbell, *Proc. Far. Soc.* 20, 379 (1925).

§ 3. RESULTS

The type of result obtained is illustrated by figures 1 and 2. These are micro-photometer records of X-ray spectra photographed under exactly the same conditions except that a screen was interposed in the incident beam when the latter was being secured. The line A is a reflection of the iron K_{α} wave-length and B of the K_{β} . The reduction of the intensity of the β lines as a result of the screen is quite apparent. The exposure to the incident beam was adjusted so as to obtain

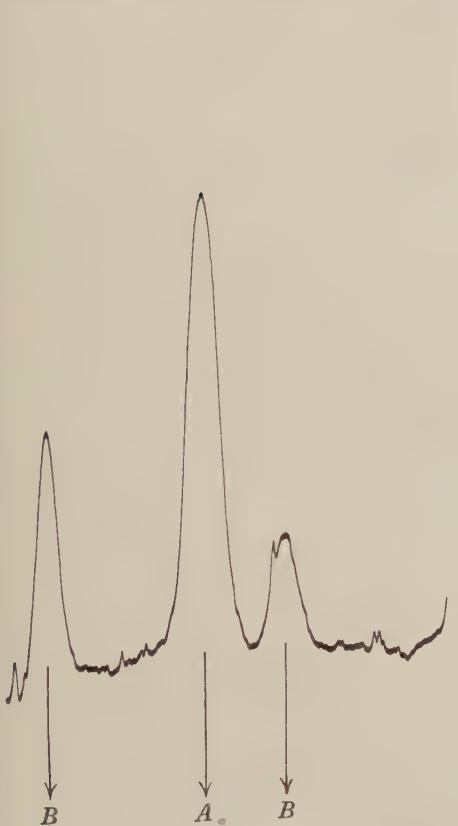


Fig. 1. Spectral intensity without screen.

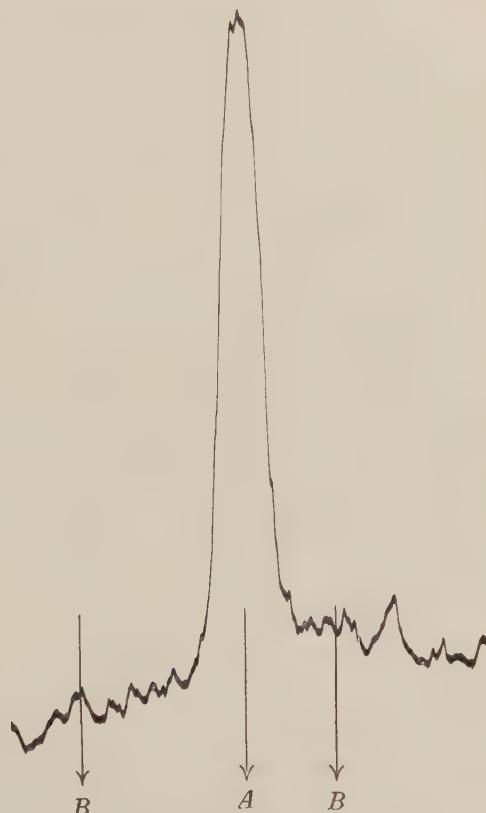


Fig. 2. Spectral intensity with screen.

as nearly as possible the same intensity of the α line in each case. The reduction of the intensity-ratio of β to α in figure 2 is thus more significant. It is possible, of course, by variation of the time of deposition to vary the efficacy of the absorbing screen. That thickness which is effective without unduly increasing the time of exposure necessary to secure a photograph can be selected by trial. It is the author's experience that such a layer will then eliminate the β lines from a photograph of normal exposure just as efficiently as nickel foil, in the better known case of copper, removes the β from the characteristic copper-radiation.

§ 4. ACKNOWLEDGMENTS

In conclusion the author expresses his thanks to Dr G. W. C. Kaye for his interest in the researches out of which the above work arose. He is very much indebted to Mr J. R. Clarkson, B.Sc., for extensive help in the preparation of the deposits.

DISCUSSION

Prof. H. R. ROBINSON. I should like to ask the author if he has made any estimates, by weighing or otherwise, of the effective thicknesses of his manganese films. He has referred to the well-known practice of filtering copper K-radiations with nickel foil; in my experience of this method, I have calculated the most suitable thickness of nickel from the available absorption data, and have subsequently found that very efficient filtration is in fact effected with foils appreciably thinner than those predicted by calculation. It seems possible that this may in part be due to the inadequacy of the absorption measurements in the immediate neighbourhood of the absorption discontinuity, and I should be interested to know if Mr Wood has had similar experiences with his manganese films.

AUTHOR'S reply. I have found, in agreement with Prof. Robinson, that the thickness of the foils necessary to filter the β -radiation is less than that indicated by theory. The effect, however, may possibly be due to the fact that the films absorb the softer radiation from the incident X-ray beam and thereby remove part of the continuous background of the photographic plate. The enhanced contrast of the spectral lines would then permit of a less exposure to secure a given visibility.

DISPLACEMENTS OF CERTAIN LINES IN THE SPECTRA OF IONIZED OXYGEN (OII, OIII), NEON (NeII) AND ARGON (AII)

BY W. E. PRETTY, A.R.C.S., B.Sc., D.I.C.

Received February 6, 1931. Read and discussed March 6, 1931.

ABSTRACT. In continuation of an investigation of the displacements which characterize certain spectral lines produced in a discharge tube at moderate gas pressure (of the order of a few cm.), the spectra OII, OIII, NeII and AII have been studied. As in the case of NII, which has been examined previously, many lines in each of the spectra are displaced to the red and for the majority of the lines the amount of displacement has been determined. The term shifts so obtained have been discussed in relation to the term schemes for each of the spectra. A comparison of the term shifts in the various spectra has been made and it is found that the $4s$ terms of OII, OIII, NII and NeII, and the $5s$ terms of AII (3P family) all show roughly the same shift. Some typical shifted lines have been examined with a microphotometer and the curves are reproduced. The suggestion made in the previous paper that the shift is probably a Stark effect receives further support.

§ 1. INTRODUCTION

In a previous paper* the shifting of certain lines of the spectrum of ionized nitrogen, caused by the raising of the gas pressure in the discharge tube, was investigated. The general nature of the results was to show that the shift was related to the terms concerned in the production of the lines, and an examination of the cause of the shift led to the conclusion that it was in the main a Stark effect. The data obtained for NII were not sufficiently extensive to do more than indicate the general nature of the effect, and it was thought that a study of other spectra might reveal a systematic relation between the displacements of the various lines and the terms associated with the lines.

With this object in view the following spectra have been investigated: OII, NeII, AII, OIII and NIII. These spectra, together with NII, provide the material for several comparisons: (1) first ionized spectra of atoms of the first row of the periodic table, NII, OII, NeII; (2) single and double ionization, OII, OIII; (3) iso-electronic systems, NII and OIII; (4) successive spectra in a vertical column of the periodic table, NeII and AII.

The spectra have in the first instance been examined separately and in considerable detail, the excitation conditions being adjusted so as to yield the best results for the particular spectrum concerned. Each spectrum has been observed under varying conditions of pressure and excitation, and varying exposures. It was found, in practice, that no great change in the electrical conditions was necessary, in passing from one gas to another, for the production of a suitable singly ionized

* *Proc. Phys. Soc. 41, 442 (1929).*

spectrum. In the case of OIII, however, it was necessary to increase considerably the violence of the discharge. The comparison of shifts in different spectra is considered later.

Many of the shifts in OII* have been recorded by Fowler, as well as some in OIII†. All those in NeII, and all those in AII‡ below $\lambda 3000$ are, as far as the author is aware, recorded for the first time.

§ 2. EXPERIMENTAL

The arrangement for producing the spectra was the same as in the first investigation. The gas was excited in an H-type tube, ordinarily made of glass, of which the capillary was about 5 cm. long and of 1 mm. bore. The exciting mechanism consisted of a 12 in. induction coil, with mercury interrupter, a condenser being included in parallel and a spark gap in series. These two latter were adjusted as was necessary to produce the required spectrum.

As before, the shifts were obtained by increase in the pressure of the gas in the discharge tube, the high pressure being in the neighbourhood of 2 cm. of mercury. The displacements were measured relative to a comparison spectrum obtained when the gas pressure was low (< 0.1 cm.). The same method was adopted of photographing overlapping regions so that the shifts in different parts of the spectra, photographed on different instruments, should be comparable with one another.

The region investigated for all the spectra was from $\lambda 6800$ to $\lambda 2300$, the instruments used being as follows:

- (1) A glass prism instrument having a dispersion of about 30 \AA/mm. at $\lambda 6800$ and 5 \AA/mm. at $\lambda 3800$.
- (2) A concave grating (Eagle mounting) with a dispersion of 5.5 \AA/mm. in the first order.
- (3) A quartz Littrow spectrograph (Hilger's EI) having a dispersion of 10 \AA/mm. at $\lambda 3800$ and 2 \AA/mm. at $\lambda 2300$.

§ 3. NOTATION

For designating a term arising from a given electron configuration, the notation as used by Fowler in papers on CH§ and OIII has been employed. For the simpler spectra, and particularly for the present purpose, it seems preferable to the more general notation recently suggested¶.

In AII three families of terms have been identified, and to distinguish between

* *Proc. R.S. A.*, **110**, 476 (1926).

† *Proc. R.S. A.*, **117**, 317 (1928).

‡ Until recently I was under the impression that all the shifts in AII were newly discovered, but it has just come to my notice that most of the lines above $\lambda 3000$ which shift have been recorded by Eder and Valenta (*Denkschriften der Math.-Nat. Klasse der K. Akad. Wiss. Wien*, 44). The shifts in their experiments resulted from the raising of the pressure of the gas in the discharge tube to 2 cm., which was roughly the same as that finally used in my argon tube. They did not, however, attempt any investigation of the shifts.

§ *Proc. R.S. A.*, **120**, 312 (1928).

¶ *Proc. R.S. A.*, **117**, 317 (1928).

¶ H. N. Russell, A. G. Shenstone and L. A. Turner, *Phys. Rev.* **33**, 900 (1929).

terms of different families arising from the same configuration of the series electron, the method used by de Bruin† has been adopted. This requires only that after the term as ordinarily expressed, e.g. $4p\ ^4D$, the family to which it belongs shall be indicated by addition as a postscript. That is, the term cited would be completely described as $4p\ ^4D\ (^3P)$ since it belongs to the family having a 3P limit‡.

In OII only two families are known and for this spectrum the simple notation is used for the main family (3P limit), e.g. $4s\ ^4P$; while the terms belonging to the 1D family have been asterisked, e.g. $*4s\ ^2D$.

Table I. Shifts in lines of OII.

λ	Int.	Classification	$d\lambda$	$d\nu$	λ	Int.	Classification	$d\lambda$	$d\nu$
§3830·45 (4)		$3p\ ^2P_2 - 4s\ ^2P_1$	—	—	3287·59 (9)		$3p\ ^4P_3 - 4s\ ^4P_3$	0·45	4·2
3821·68 (4)		$P_1 - P_1$	0·53	3·7	3277·69 (7)		$P_2 - P_3$	0·44	4·1
3803·14 (6)		$P_2 - P_2$	0·60	4·1					
3794·48 (3)		$P_1 - P_2$	0·56	3·9	‡3273·52 (7)		$*3p\ ^2F_4 - *4s\ ^2D_3$	0·45	4·2
					‡3270·98 (7)		$F_3 - D_2$	0·46	4·3
3777·60 (4)		$3p\ ^1S_2 - 4s\ ^1P_1$	0·59	4·1	3139·77 (4)		$3p\ ^4D_2 - 4s\ ^1P_1$	0·41	4·2
3762·63 (5)		$S_2 - P_2$	0·56	3·9	3138·44 (8)		$D_3 - P_2$	0·37	3·8
3739·92 (6)		$S_2 - P_3$	0·58	4·1	3134·82 (10)		$D_4 - P_3$	0·41	4·2
3735·94 (3)		$*3p\ ^2P_2 - *4s\ ^2D_{32}$	0·51	3·7	§3134·32 (3)		$D_1 - P_1$	—	—
§3729·34 (2)		$P_1 - D_{32}$	—	—	3129·44 (7)		$D_2 - P_2$	0·42	4·3
					3124·02 (2)		$D_1 - P_2$	—	—
3470·81 (8)		$3p\ ^2D_3 - 4s\ ^2P_2$	0·54	4·5	3122·62 (6)		$D_3 - P_3$	0·40	4·1
3470·42 (5)		$D_2 - P_1$	—	—	3113·71 (1)		$D_2 - P_3$	—	—
§3447·98 (5)		$D_2 - P_2$	—	—					
3409·84 (6)		$*3p\ ^2D_2 - *4s\ ^2D_{32}$	0·48	4·1	2747·46 (6)		$3p\ ^2S_1 - 4s\ ^2P_1$	0·44	5·8
§3407·38 (7)		$D_3 - D_{32}$	—	—	2733·34 (10)		$S_1 - P_2$	0·43	5·8
3306·60 (6)		$3p\ ^4P_2 - 4s\ ^4P_1$	0·41	3·8	2718·84 (2)		$+2p\ ^2S_1 - 3p\ ^2P_1$	0·14	1·9
3305·15 (6)		$P_3 - P_2$	0·46	4·2	2715·38 (3)		$S_1 - P_2$	0·15	2·0
§3301·56 (3)		$P_1 - P_1$	—	—					
3295·13 (4)		$P_2 - P_2$	0·45	4·1	2436·10 (4n)			0·25	4·2
3290·13 (5)		$P_1 - P_2$	0·43	4·0	2425·62 (5n)			0·24	4·1
					2406·41 (3n)			0·22	3·8

* Based on 1D state of core.

† Arises from the configuration sp^4 . See figure I.

‡ Classification by Russell.

§ High-pressure line confused.

|| Shift observable but not measurable.

§ 4. OXYGEN

The spectrum of singly ionized oxygen, OII. The spectrum has been investigated very fully by A. Fowler§, and an interpretation of the experimental results on the basis of Hund's theory has been given by R. H. Fowler and Hartree||. The analysis has been extended by Bowen¶ who identified the deepest terms thereby deter-

† Proc. Acad. Amsterdam, 33, 198 (1930).

‡ It would be more logical to introduce the family designation between the electron symbol ($4p$) and the term type (4D), but it seems to the author that in the method adopted the list of lines is more easily readable.

§ Proc. R.S. A, 110, 476 (1926).

|| Proc. R.S. A, 111, 83 (1926).

¶ Phys. Rev. 29, 242 (1927).

mining the ionization potential. Later, Russell* has identified many of the higher terms predicted by theory, and has also identified intercombinations, thus fixing definitely the values of the quartet terms which had previously been given an arbitrary starting-point by A. Fowler.

The wave-lengths and classifications are taken from those published by A. Fowler, the only change being in the notation.

In the case of OII, up to the present there have been identified two families of terms. The first, consisting of doublet and quartet terms, arises from the addition of an electron to a core in which the electrons outside the completed K shell have the configuration $s^2 p^2$, the limiting value of the family being the 3P term of OIII.

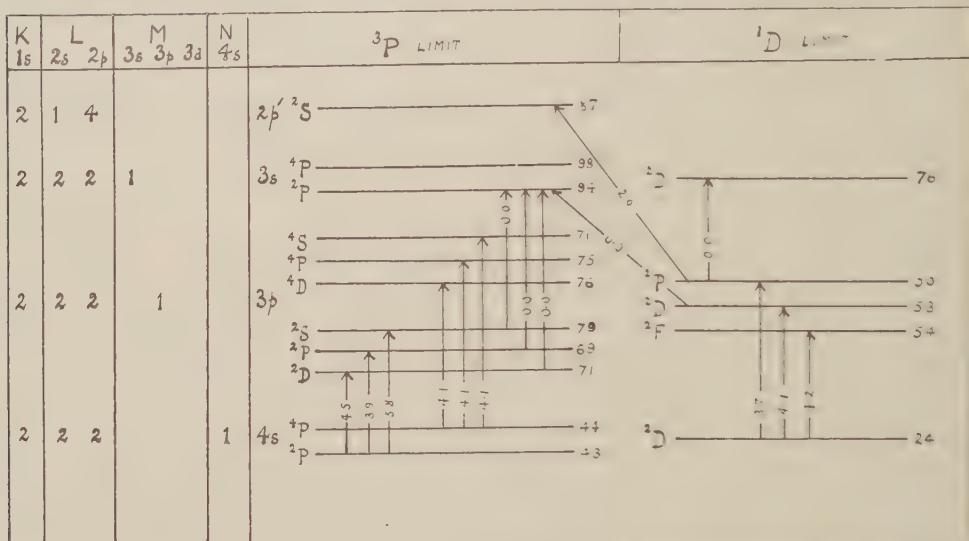


Fig. 1. Term scheme for OII.

This is usually referred to as the main family. The second is a family of doublets only and arises similarly but has as limit the 1D term of OIII. A third system with limit 1S is predicted by theory, but no terms have yet been definitely assigned to it. One term based on a different configuration of the electrons outside the K shell, viz. sp^4 , is distinguished by a dash, e.g. $2p' ^2S$.

Table 1 contains the lines which have been observed to show large shifts, together with the measured shifts. In all cases the shift is to the red. With a few exceptions the lines have been recorded as unsteady lines by A. Fowler. The shifted lines are more or less symmetrical but there is a slight shading to the red. A portion of the spectrum is reproduced in the plate. Most of the shifts have been measured, and it will be observed that the lines of a given multiplet all show the same shift to the order of accuracy of the measurements.

The term scheme for OII and approximate term values (in thousands of cm.⁻¹) are shown in figure 1. The scheme is not at all complete but is sufficiently so

* *Phys. Rev.* 81, 27 (1928).

for the present purpose. Transitions and corresponding shifts are indicated by arrows. The shift inserted is the mean of the shifts of the lines constituting the multiplet.

Combinations between terms each having total quantum number n equal to 3 are steady, while those between terms having n equal to 4 and those with n equal to 3 all show a pronounced shift. Moreover the doublet and quartet terms with 3P limit show approximately the same shift, with the exception of $4s\ ^2P$ when combining with $3p\ ^2S$. The terms having limit 1D are much smaller than the corresponding terms with limit 3P , but they show much the same shift as the $4s - 3p$ combinations of the main family.

In the previously investigated spectrum, NII, no transitions from a term of total quantum number 3 to one of total quantum number 2 fell within the observed range, and it was accordingly assumed that terms having n equal to 3 were stable. In OII, however, the combination $2p'\ ^2S - 3p\ ^2P$ is observable and is found to shift. Thus the absence of shift in lines associated with $3p$ to $3s$ transitions is probably due not to the absence of any effect on these terms but to the equality of the perturbations. If we assume that the term shift is really a property of the term under given conditions, it would appear from the diagram that if those terms are steady which have n equal to 2 the shift in terms with n equal to 3 is 2 frequency units and in terms with n equal to 4 it is 6 units. What is determined by experiment is the relative shift between two terms, and it must still be borne in mind that even this is determined by the exciting conditions, increasing as the pressure increases with a given discharge tube. Shifts were measured with the gas at various pressures and, for the same spark gap and condenser, the shift increased with the pressure as in the case of NII. For the shifts given in table I the pressure was about 1.0 cm., spark gap in series 3.0 mm. (1.5-cm. spheres) and condenser 0.005 μ F. This was found the most suitable arrangement for obtaining the best results.

Most of the lines assigned by Russell* to terms involving total quantum numbers 4 and 5 fall in the observed region, but many of them are too weak, on the plates so far obtained, for decision whether they show a shift or not. There are a few strong lines, however, viz. $\lambda 4087.16$, $\lambda 4253.98$ and two groups, one consisting of 6 lines at $\lambda 4280$ and the other of 3 lines at $\lambda 4290$, which are associated with terms having n equal to 4 ($4f$) and yet do not shift to any observable extent. These lines are inherently somewhat diffuse, and this militates against the observations, but there seems little doubt that these lines do not show the same type of shift as shown by the $4s$ terms. This is surprising in the light of the results already obtained for NII, where the shift of the $4p$ and $4d$ terms was of the same order as that of the $4s$ terms. (Unfortunately no $4f$ terms in NII have yet been identified.) Lines involving Russell's $5f$ terms are not visible in the high-pressure spectrum, this being probably due to their becoming very diffuse.

The three unclassified lines which are given in the list are quite strong and shift in the same way as the others, but have so far evaded classification.

* Loc. cit.

It was thought that the anomaly of the $4s\ 2P$ term in combination with $3p\ 2S$ might be due to the latter term being affected to a lesser extent than the $2P$ and $2D$ terms arising from the $3p$ configuration. When each of these terms combines with terms arising from the $3p\ 2P$, however, the resulting lines are all steady, and it would appear as if the behaviour of the $4s\ 2P$ term in the $3p\ 2S - 4s\ 2P$ transition is really anomalous, as the $4d\ 3P$ term in NII appears to be.

The spectrum of doubly ionized oxygen, OIII. It was necessary to use a longer spark gap and larger capacity for producing the doubly ionized spectrum of oxygen. In order to measure the shifts it was also necessary that a rather lower pressure should be used. In addition, a quartz tube of narrower bore was employed instead

Table 2. Shifts in lines of OIII.

λ	Int.	Classification	$d\lambda$	$d\nu$	λ	Int.	Classification	$d\lambda$	$d\nu$
†2713.40	(2)	$3d\ 3P_0 - 4p\ 3D_1$	—	—	†2453.54	(2n)	$3d\ 3P_1 - 4p\ 3P_0$	—	—
†2708.87	(1)	$P_1 - D_1$	—	—	†2451.91	(2n)	$P_0 - P_1$	—	—
†2701.05	(3)	$P_1 - D_2$	—	—	†2448.21	(1n)	$P_1 - P_1$	—	—
†2692.74	(1)	$P_2 - D_2$	—	—	†2441.72	(2n)	$P_1 - P_2$	—	—
†2677.81	(3n)	$P_2 - D_3$	—	—	†2441.41	(oo)	$P_2 - P_1$	—	—
					†2434.96	(2n)	$P_2 - P_2$	—	—
2609.59	(4)	$3d\ 3P_0 - 4p\ 3S_1$	0.23	3.4					
2605.41	(6)	$P_1 - S_1$	0.22	3.2					
2597.69	(8)	$P_2 - S_1$	0.25	3.7	2438.83	(5n)	$3d\ 1P_1 - 4p\ 1D_2$	0.15	2.6
					2422.84	(5n)	$3d\ 1F_3 - 4p\ 1D_2$	0.14	2.5
2558.06	(8)	$3p\ 1P_1 - 4s\ 1P_1$	0.25	3.8					
†2549.62	(2)	* $3d\ 3D_2 - 4p\ 3D_1$	—	—	†2394.33	(5n)	$3d\ 1P_1 - 4p\ 3D_1$	0.19	3.3
†2547.45	(2)	$D_3 - D_2$	—	—	†2388.20	(1)	$P_1 - D_2$	—	—
2546.43	(4)	$D_1 - D_1$	0.24	3.6	2383.92	(6n)	$3d\ 3F_3 - 4p\ 3D_2$	0.19	3.4
2542.68	(5)	$D_2 - D_2$	0.20	3.0	2382.32	(7n)	$F_4 - D_3$	0.20	3.6
†2539.50	(2)	$D_1 - D_2$	—	—	2378.90	(4n)	$F_2 - D_1$	0.21	3.6
2534.08	(6n)	$D_3 - D_3$	0.18	2.8	†2372.82	(2n)	$F_2 - D_2$	—	—
†2529.36	(1)	$D_2 - D_3$	—	—	†2372.21	(3n)	$F_3 - D_3$	—	—

* In Fowler's paper this term is misprinted $3p\ 3D_2$.

† These lines could be seen to be displaced but were not measurable in the high-pressure spectrum.

‡ Not visible in high-pressure spectrum.

of the glass one used for the other spectra. Even so it was much more difficult to obtain plates suitable for measurement and the measured shifts are not considered as accurate as those in OII. The difficulty was the same as that experienced in a much lesser degree in the other spectra, viz. the diffuseness of the lines in the high-pressure spectrum and the continuous background always associated with the high-pressure spectrum.

Two fairly satisfactory plates were eventually obtained and the means of the shifts on the two plates are given in table 2*. The wave-lengths and classifications

* The values given in table 2 are not actually the measured shifts, but are the latter multiplied by 1.10. This plan has been adopted because the OII lines occurring on the plates used for measuring the OIII lines showed shifts equal to 1.110 of the values given in table 1. Hence to make the two sets of oxygen shifts comparable the OIII shifts were multiplied by 1.10. This question of comparing the shifts in different spectra is considered later in the paper.

are those of Fowler*. About half only of the observed shifts have been measured. In some groups the faintest lines were not visible in the high-pressure spectrum, but as no instance has yet been found in which the lines of a group behave differently these faint lines have been included in the list for completeness and to avoid any ambiguity.

The term scheme for OIII is represented in figure 2, and the term shifts have been inserted as in the previous diagram for OII. As in NII and OII lines arising from transitions from terms having n equal to 4 to those having n equal to 3 are shifted in the high-pressure spectrum, while lines associated only with terms for which $n = 3$ are steady. Unfortunately lines arising from $3 \rightarrow 2$ transitions are out of range.

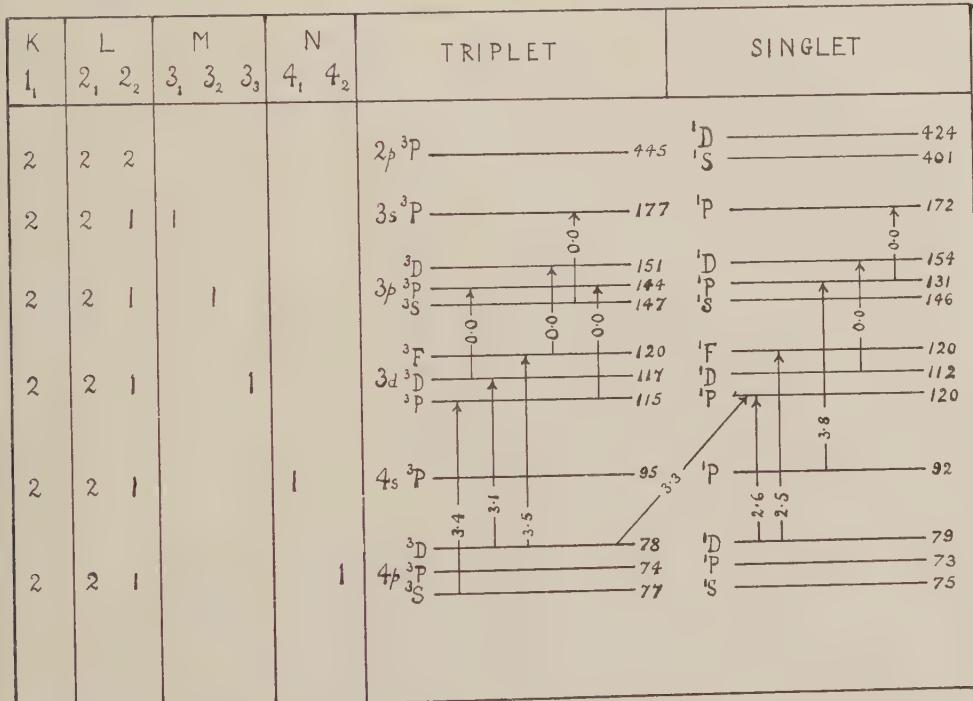


Fig. 2. Term scheme and shifts in OIII.

§ 5. NITROGEN

The spectrum of doubly ionized nitrogen, NIII. Some shifting lines on the plates taken for the investigation of NII were at first thought to be due to NIII but do not find a place in the list given by Freeman†, and their origin is not yet known. No large shifts in any of the lines which are known to be due to NIII have yet been observed, but the lines which might be expected to shift are weak and are not visible in the high-pressure spectra on the plates so far obtained.

* Proc. R.S. A, 117, 317 (1928).

† Proc. R.S. A, 121, 318 (1928).

§ 6. NEON

The spectrum of neutral neon, NeI . In view of the fact that many of the lines of the spectrum of neutral neon have been adopted as secondary standards* in the yellow-red region, it was considered appropriate to the investigation of the "pressure effect" to see whether any of the lines concerned were appreciably affected, when the pressure of the gas in a tube excited as in the foregoing experiments was increased. This was carried out with pressures up to 15 cm., this pressure being much higher than had been possible for nitrogen or oxygen.

Table 3. Shifts in lines of $NeII$.

Classified lines. Large shifts					Classified lines. Small shifts (cont.)				
λ	Int.	Classification	$d\lambda$	$d\nu$	λ	Int.	Classification	$d\lambda$	$d\nu$
*3397·81	(1)	$3p\ ^4S_2 - 4s\ ^4P_2$	—	—	3054·70	(5)	$3p\ ^4P_1 - 3d\ ^4D_2$	0·19	2·0
*3362·90	(1)	$S_2 - P_1$	—	—	3047·60	(6)	$P_2 - D$	0·20	2·1
					3045·56	(3)	$P_1 - D_1$	0·18	1·9
*3072·68	(1)	$3p\ ^4D_1 - 4s\ ^1P_2$	—	—	3037·75	(3)	$P_2 - D_2$	0·19	2·0
*3059·15	(3)	$D_2 - P_2$	—	—	3034·49	(5)	$P_3 - D_4$	0·19	2·0
*3044·10	(2)	$D_1 - P_1$	—	—	3027·07	(4)	$P_2 - D_1$	0·17	1·9
†3039·62	(4)	$D_4 - P_3$	0·71	7·7	3017·36	(3)	$P_3 - D_2$	0·16	1·8
*3035·95	(2)	$D_3 - P_2$	—	—	2910·44	(2)	$3p\ ^4P_1 - 3d\ ^4P_1$	0·16	1·8
*3030·82	(2)	$D_2 - P_1$	—	—	*2906·85	(1)	$P_1 - P_2$	—	—
2809·51	(4)	$3p\ ^4P_2 - 4s\ ^4P_3$	0·54	6·9	2872·96	(2)	$P_3 - P_2$	0·13	1·6
2794·22	(3)	$P_1 - P_2$	0·58	7·4	2869·93	(1)	$P_3 - P_3$	0·16	1·9
2792·04	(4)	$P_3 - P_3$	0·57	7·4					
2780·05	(2)	$P_2 - P_2$	0·60	7·7	2876·41	(3)	$3p\ ^4P_2 - 3d\ ^4F_2$	0·16	2·0
2770·63	(1)	$P_1 - P_1$	0·55	7·2	2858·02	(1)	$P_3 - F_2$	0·16	2·0
2762·97	(3)	$P_3 - P_2$	0·59	7·7					
2756·68	(3)	$P_2 - P_1$	0·58	7·6					
Unclassified lines									
Classified lines. Small shifts					3164·42	(3)	—	0·19	1·9
3194·58	(4)	$3p\ ^4D_2 - 3d\ ^4P_2$	0·21	2·1	3197·15	(2)	—	0·23	2·4
3173·58	(3)	$D_3 - P_1$	0·19	1·9	3093·99	(4)	—	0·77	8·0
3165·68	(2)	$D_3 - P_3$	0·22	2·2	3092·91	(2)	—	0·27	2·8
3176·14	(3)	$3p\ ^4D_2 - 3d\ ^4F_2$	0·28	2·8	3088·16	(3)	—	0·77	8·0
3118·00	(4)	$D_1 - F_3$	0·26	2·7	2967·20	(3)	—	0·67	7·6
					2963·29	(2)	—	0·57	6·5
					2933·71	(1)	—	0·16	1·8

* Shift visible but not measurable.

† Slightly confused in high-pressure spectrum.

No shift of the type already found was observed, but at the higher pressures the lines became much broader and the broadening was asymmetrical, being greater to the red. At pressures of 1 cm. and less no pronounced broadening was observed. In the use of the lines as standards it is arranged to have the pressure very much lower than this so that there can be no doubt as to their freedom from "pressure effect."

The spectrum of singly ionized neon, $NeII$. By increase of the violence of the discharge the first ionized spectrum of neon was easily produced, and it was photo-

* Trans. Int. Ast. Union, 3, 10, 18 (1928).

graphed over the region $\lambda 6800-\lambda 2300$ although the examination has been less exhaustive than that of any of the other spectra. Owing to the fact that the lines were much better separated, a higher pressure than for nitrogen or oxygen could conveniently be used, not so much for obtaining better measures of the large shifts as for detecting smaller ones. The pressure used was 5.0 cm. and the series gap was increased to 0.6 cm.

In the region over which photographs have been taken only twelve lines showing large shifts have been measured, but there occurred many lines showing small but quite definite shifts, and, with the high pressure that it was possible to use, these were measurable. The shifting lines are given together with the measured shifts in table 3. All the shifts are to the red.

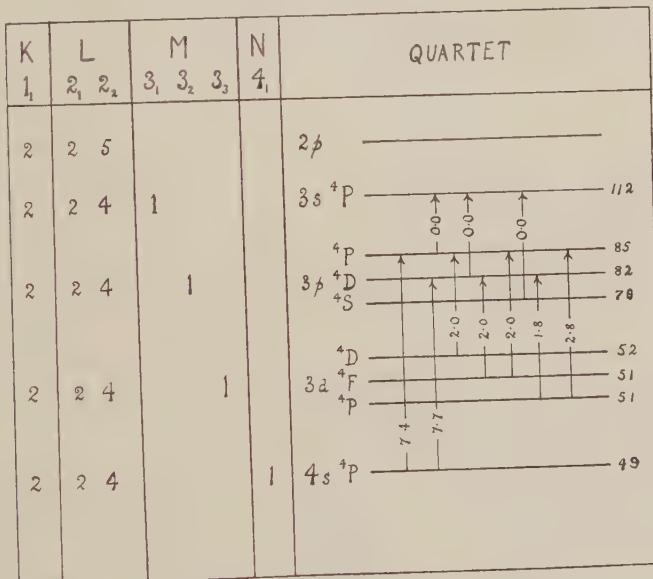


Fig. 3. Term scheme and shifts in NeII.

The wave-lengths are by L. Bloch and G. Dejardin* and the classifications are by de Bruin†. It will be observed that all the lines showing large shifts are, with four exceptions, associated with the quartet P term arising from the $4s$ level. The four remaining lines are as yet unclassified. The $4s^4P$ term behaves then similarly to the corresponding terms in OII and NII. In the occurrence of many lines showing small shifts, the spectrum differs from OII and NII. These lines are all due to transitions between $3d$ terms and $3p$ terms, which in the two other spectra were steady. This may be partly due to the higher pressure used for neon spectra, making the detection of small shifts easier, but is certainly not due entirely to this cause.

* *Journ. d. Phys.*, 7, 129 (1926).

† *Proc. Acad. Amsterdam*, 31, 2 (1928) and *Archives Néerlandaises des Sciences*, 2, 132 (1928).

It should perhaps be explained here how the descriptions large and small are used. It will be observed by reference to table 3 that the so-called "small shifts" are about 2 cm^{-1} , and this is actually of the same order as the "large shifts" in the NII spectrum. It will be seen later, however, that when produced in the same tube the "small" neon shifts are only about one-quarter of the nitrogen shifts, and are therefore really small compared to the NII shifts. Under these conditions the shifts in the lines of the $4s\ 4P$ term in NeII, which in table 3 are rather more than 7 cm^{-1} , are somewhat less than those of the $4s\ 3P$ term in NII.

The term scheme and transitions in NeII are represented in figure 3. Only the quartet terms have yet been identified. It seems likely that some of the lines having large shifts, and not yet classified, belong to the $4s\ 2P$ term, but no definite assignment has been attempted. Of the classified lines all but one of those showing large shifts are associated with the combination $3p\ 4P - 4s\ 4P$, and the shifts are equal within the limits of accuracy of the measurements. The other line arises from the $3p\ 4D - 4s\ 4P$ combination, and shows the same shift as the lines of the $3p\ 4P - 4s\ 4P$ group. The remaining lines in this group could be seen to shift but were too faint for measurement.

In the $3d \rightarrow 3p$ transitions the shifts are equal, except in the case of the $3d\ 4F$ term, which shows a larger shift in combination with $3p\ 4D$ than it does when in combination with $3p\ 4P$. A similar double behaviour has already been noticed in the $4d\ 3P$ term of NII, and the $4s\ 4P$ term of OII.

§ 7. ARGON

Singly ionized argon, AII. The classifications used in the investigation of the shifts in the spectrum of singly ionized argon are those of de Bruin*. In the first paper cited he identified most of the terms of the main family (3P limit), resulting from the addition to the core of a $3d$, $4s$, $4p$, $4d$ and $5s$ electron. The present work was almost completed when the second paper quoted appeared. In this many of the terms belonging to the families having limits 1D and 1S have been identified, resulting in the classification of a great many more lines. For the second analysis de Bruin made use of the very full list of wave-lengths recently published by Rosenthal†, and these have for the main part been used in the present paper.

Of the lines that have been found to shift, by far the greater number belong to the main family. Shifting lines belonging to each of the other two families have also been found, and the results obtained are much more complete than those for any of the other spectra investigated. The lines that have been observed to shift and the measured shifts are collected in table 4. The region investigated was from $\lambda 6800$ to $\lambda 2300$ although no large shifts have been observed above $\lambda 4800$, with the exception of three unclassified lines, $\lambda 5847$, $\lambda 5929$, $\lambda 5819$. Between $\lambda 4800$ and $\lambda 3000$ the list of lines published by Rosenthal agrees very well with the plates taken during the present work, but below $\lambda 3000$ the intensities of the lines on the

* *Proc. Acad. Amsterdam*, 31, 771 (1928); 33, 198 (1930).

† *Ann. d. Physik.* 4, 49 (1930).

λ	Int.	Classification	$d\lambda$	$d\nu$	λ	Int.	Classification	$d\lambda$	$d\nu$
4721·62 (4)		$4p^4S_2(^3P) - 5s^4P_2(^3P)$	1·35	6·1	4420·94 (4)		$3d^4D_1(^3P) - 4p^4D_2(^3P)$	0·15	0·8
4733·36 (4)		$3d^2P_1(^1D) - 5p^2P_2(^1D)$	0·83	3·8	4352·20 (5)		D_1	0·15	0·8
*4598·77 (5)		$3d^2D_2(^3P) - 4p^2P_2(^1D)$	0·51	2·4	4332·04 (5)		D_2	0·16	0·8
*4474·77 (6)		D_1	1·28	5·8	4099·47 (3)		$4p^2P_1(^3P) - 3d^2S_1(^1D)$	0·15	0·9
+4564·43 (5)		$4p^4S_2(^3P) - 5s^4P_2(^3P)$	—	—	4038·82 (4)		$3d^4D_3(^3P) - 4p^4D_4(^3P)$	0·14	0·9
+4547·78 (5)		$4p^2P_2(^3P) - 5s^4P_2(^3P)$	—	—	4013·85 (8)		D_4	0·14	0·9
*4502·95 (5)		$4p^2D_2(^3P) - 5s^4P_3(^3P)$	0·59	2·9	3992·05 (4)		D_2	0·15	1·0
4498·55 (5)		$3d^2P_2(^1D) - 5p^2D_3(^1D)$	0·76	3·4	3968·35 (5)		D_3	0·13	0·8
4448·88 (6)		$4p^2D_3(^1D) - 3d^2D_3(^1S)$	1·12	5·1	3944·26 (4)		D_4	0·14	0·9
4440·09 (3)		D_2	—	—	3891·98 (4)		D_3	0·12	0·8
4439·45 (3)		D_2	—	—	3891·40 (3)		D_1	—	—
+4433·83 (5)		$3d^2D_3(^1D) - 5p^2F_4(^1D)$	0·68	3·1	4031·41 (2)		$4p^2D_2(^3P) - 4d^4D_2(^3P)$	—	—
+4379·74 (8)		$4p^2S_1(^3P) - 5s^2P_1(^3P)$	—	—	3988·18 (4)		D_3	0·84	5·3
*4277·55 (8)		$4s^2D_3(^1D) - 4p^2P_2(^1D)$	0·46	2·5	3958·39 (5)		D_3	0·80	5·1
*4237·23 (7)		$4s^2D_2(^3P) - 5s^2P_2(^3P)$	0·39	2·2	3979·36 (7)		D_3	—	—
4275·19 (4)		$4p^2P_1(^3P) - 5s^2P_2(^3P)$	—	—	3932·55 (7)		$4p^4S_2(^3P) - 4d^4P_1(^3P)$	0·77	4·9
4222·67 (5)		P_2	—	—	3952·74 (6)		S_2	0·78	5·0
4129·70 (4)		P_1	—	—	3946·10 (7)		$4p^4S_2(^3P) - 4d^4F_2(^3P)$	0·79	5·0
4218·69 (5)		$4p^2D_2(^3P) - 5s^2P_2(^3P)$	0·94	5·3	3925·71 (3)		$4p^2F_4(^1D) - 3d^2D_3(^1S)$	0·83	5·3
*4420·58 (2)		$4p^4D_1(^3P) - 5s^4P_2(^3P)$	0·59	3·3	3911·58 (5)		F_1	0·80	5·2
4179·31 (5)		D_3	—	—	3900·63 (5)		D_2	—	—
4156·11 (5)		D_2	—	—	3886·34 (4)		D_1	0·55	3·7
4103·91 (10)		D_4	—	—	3872·15 (5)		D_2	0·54	3·6
4076·64 (5)		$[4p^2D_3 - 5s^2P_2]$	0·99	5·9	3844·75 (4)		D_3	—	—
4072·49 (7)		$4D_1$	—	—	3841·54 (3)		D_2	0·51	3·5
4033·83 (6)		D_3	—	—	3826·83 (6)		D_1	0·58	4·0
*4131·73 (8)		D_2	—	—	3799·39 (6)		D_3	—	—
+4082·40 (6)		$4s^2D_2(^1D) - 4p^2P_1(^1D)$	0·86	5·0	3788·84 (8)		D_4	0·60	4·2
		$[4p^2P_2(^3P) - 4d^2D_3(^3P)]$	—	—	3763·52 (5)		D_3	0·58	4·1
		$[4s^2P_3(^3P) - 4p^2D_3(^3P)]$	—	—	3825·70 (6)		D_2	—	—
		$[4s^2P_3(^3P) - 4p^2D_3(^3P)]$	—	—	3803·19 (6)		D_3	0·88	6·1

† Shift visible but not measurable.

* Classification doubtful (or possibly two lines present).

† The line corresponding to $3d^2D_2(^1D) - 5p^2D_2(^1D)$ should also occur here and the shift is consistent with this classification. If the line corresponding to de Bruin's classification is present it must be much weaker than $3d^2D(^1D) - 5p^2D_2(^1D)$.

Table 4 (cont.).

λ	Int.	Classification	$d\lambda$	$d\nu$	λ	Int.	$d\lambda$	$d\nu$
3809.49	(7)	$4p^4P_2(^3P) - 5s^4P_3(^3P)$	0.77	5.3	3535.33	(6)	$4p^4P_1(^3P) - 4d^4D_2(^3P)$	0.54
3770.54	(6)	P_1^-	0.80	5.6	3514.39	(9)	P_1^2	0.56
3765.27	(6)	P_3^-	0.85	6.0	3509.78	(6)	D_1^-	0.46
3720.43	(5)	P_3^-	—	P_3^-	3491.54	(8)	D_4^-	3.8
3678.27	(5)	P_2^-	—	P_2^-	3491.24	(6)	P_3^2	4.2
3622.15	(6)	P_2^-	0.74	5.6	3476.74	(6)	P_3^2	0.50
[†] 3754.06	(3)	$4p^2P_1(^1D) - 4d^2P_1(^1D)$	—	—	3466.34	(5)	D_3^-	4.2
[†] 3753.53	(4)	$4p^2P_1(^1D) - 4d^2P_2(^1D)$	—	—	3454.10	(5)	D_1^-	3.4
3737.89	(6)	$4p^2D_3(^1D) - 4d^2F_4(^1D)$	0.89	6.4	3388.54	(7)	$4p^2S_1(^3P) - 4d^2P_2(^3P)$	0.52
3718.21	(6)	D_2^-	0.72	5.2	§3376.46	(7)	$4p^2F_4(^1D) - 4d^2F_4(^1D)$	—
3660.44	(6)	$4p^2P_2(^1D) - 4d^2D_2(^1D)$	0.74	5.5	3350.94	(6)	F_3^-	0.60
3655.29	(6)	$4p^2P_2(^3P) - 4d^2F_3(^3P)$	0.70	5.2	†3366.59	(4)	$4p^2P_2(^3P) - 4d^2P_1(^3P)$	—
3650.90	(4)	$4p^4P_1(^3P) - 5s^2P_2(^3P)$	0.73	5.5	§3307.24	(6)	P_1^-	0.50
3622.15	(6)	P_1^2	0.74	5.6	§3293.66	(7)	P_1^2	0.46
3603.91	(3)	P_2^-	0.73	5.6	†3230.82	(4)	P_2^-	—
3588.44	(10)	$4p^4D_1(^3P) - 4d^1F_5(^1P)$	0.72	5.6	3288.72	(6)	$4p^4P_1(^3P) - 4d^4P_1(^3P)$	0.49
3582.35	(8)	D_2^-	0.70	5.4	3249.82	(7)	P_1^2	0.54
[†] 3581.62	(6)	D_1^-	—	D_1^-	3243.70	(7)	P_1^2	0.52
3576.62	(10)	D_3^-	0.72	5.6	3180.05	(7)	P_2^2	0.54
3548.51	(5)	D_2^-	0.52	4.2	3169.68	(8)	P_3^2	5.1
3521.27	(5)	D_1^-	0.65	5.2	¶ 3273.36	(4)	$4p^2D_2(^3P) - 4d^2P_1(^3P)$	—
3520.00	(6)	F_3^-	0.62	5.0	3204.34	(5)	D_2^-	0.49
3565.02	(5)	$4p^4D_1(^3P) - 4d^1F_5(^1P)$	0.60	4.8	1326.60	(5)	$4p^4P_1(^3P) - 4d^2F_2(^3P)$	—
3421.64	(5)	D_3^-	0.56	4.8	3194.25	(5)	F_2^-	0.56
3370.97	(5)	D_4^-	—	D_4^-	—	—	—	5.4
3561.04	(6)	$4p^2P_1(^1D) - 4d^2G_3(^1D)$	0.64	5.1	¶ 3103.38	(4)	$4p^2S_1(^3P) - 4d^2D_2(^3P)$	0.26
3545.84	(8)	P_3^-	0.72	5.7	* 2979.05	(6)	$4p^2P_1(^1D) - 4p^2P_1(^1D)$	0.36
3559.53	(6)	$4p^2D_3(^3P) - 4d^2F_4(^3P)$	0.70	5.4	* 2891.61	(5)	P_1^-	4.1
3464.14	(6)	D_3^-	0.60	5.0	—	—	0.33	3.9

* Classification doubtful (or possibly two lines present).

[†] Shift visible but not measurable.‡ The line corresponding to $3d^2D_2(^1D) - 5p^2D_2(^1D)$ should also occur here and the shift is consistent with this classification. If the line corresponding to de Bruin's classification is present it must be much weaker than $3d^2D_2(^1D) - 5p^2D_2(^1D)$.

§ High-pressure line confused.

Table 4 (cont.).

λ	Int.	Classification	$d\lambda$	d_ν	λ	Int.	Classification	$d\lambda$	d_ν
†2960·27	(4)	—	—	—	2768·28	(5)	—	—	3·2
†2931·49	(4)	—	—	—	†2708·12	(5)	—	—	—
2896·75	(+) (0)	—	—	—	2647·29	(3)	—	—	—
2775·97	(0)	—	—	—	2592·12	(0)	—	—	—
2769·74	(4)	—	—	—	2591·51	(2)	—	—	—
2767·40	(6)	4s 1P_3 (3P)	—	—	2584·89	(3)	—	—	—
*2764·66	(3)	—	—	—	2576·40	(2)	—	—	—
2744·82	(4)	—	—	—	2570·46	(2)	—	—	—
2732·53	—	—	—	—	—	—	—	—	—

The following wave-lengths are by the author:

λ	Int.	ν	Classification	$d\lambda$	d_ν	λ	Int.	ν	Classification	$d\lambda$	d_ν
†2506·55	(3)	3988·9	—	—	—	†2427·52	(2)	4118·8	—	—	—
†2504·39	(3)	3991·7	—	—	—	†2427·24	(2)	4116·5	—	—	—
2496·43	(3)	4004·5	—	—	—	†2426·20	(2)	4120·4	—	—	—
†2494·87	(3)	4007·0	—	—	—	†2425·51	(5)	4121·5	—	—	—
†2488·88	(4)	4016·6	—	—	—	†2424·54	(1)	4123·2	—	—	—
2476·55	(3)	4026·6	—	—	—	†2424·32	(3)	4123·6	—	—	—
2476·07	(3)	4037·4	—	—	—	†2423·98	(5)	4124·1	—	—	—
2472·96	(5)	4042·5	—	—	—	2423·55	(5)	4124·9	—	—	—
2471·91	(3)	4044·2	—	—	—	2419·98	(4)	4131·0	—	—	—
2468·70	(4)	4049·4	—	—	—	†2418·87	(5)	4132·9	—	—	—
†2464·59	(2)	4056·2	—	—	—	†2416·04	(4)	4137·7	—	—	—
†2464·27	(2)	4056·7	—	—	—	†2415·90	(4)	4137·9	—	—	—
†2463·00	(2)	4058·6	—	—	—	†2415·67	(4)	4138·3	—	—	—
†2457·98	(2)	4067·1	—	—	—	2413·25	(6)	4142·5	—	—	—
2454·59	(4)	4072·7	—	—	—	2411·05	(5)	4146·3	—	—	—
2443·65	(3)	4091·0	—	—	—	2410·87	(5)	4146·6	—	—	—
2441·25	(3)	4095·2	—	—	—	2410·39	(3)	4147·4	—	—	—
2438·79	(7)	4099·5	—	—	—	2405·02	(4)	4156·7	—	—	—
2436·81	(5)	4102·8	—	—	—	†2404·59	(3)	4157·4	—	—	—
2432·79	(6)	4109·2	—	—	—	2399·22	(6)	4166·7	—	—	—
2431·57	(4)	4113·2	—	—	—	2395·67	(5)	4172·9	—	—	—

* Classification doubtful (or possibly two lines present).

† Shift visible but not measurable.

present plates show considerable divergence from those given by Rosenthal. Furthermore many of the shifting lines below $\lambda 2500$ are not given in Rosenthal's list, so that below this wave-length the values given in the table are determined from the plates taken for this investigation. Most of the shifting lines in this region are unclassified, but there is little doubt that they are due to argon; probably AII, possibly AIII.

§ 8. EFFECT OF INTENSITY ON THE MEASURED SHIFT

In the previously considered spectra NII, OII, and NeII, it was found that the measured shifts were not much affected by the length of exposure, but in the case of AII considerable variation, according to the exposure, was found in the measured shifts of a few strong lines, the shift increasing with increased exposure. It was also noticed that whereas in the other spectra all the lines of a multiplet showed the same shift, in a few multiplets in AII, notably among them $4p^4D - 4d^4F$, the lines showed different shifts, the strongest lines showing the largest shifts. By suitably arranging the length of exposure, however, the shifts were found to be more or less equal. The following list (table 5) shows how the shifts varied under different conditions.

Table 5.

λ	Int.	$d\lambda$		Classification
		(i)	(ii)	
3588·44	(10)	0·83	0·57	$4p^4D_4(^3P) - 4d^4F_5(^3P)$
3582·35	(8)	0·63	0·52	D_3 — F_3
3576·62	(10)	0·72	0·56	D_3 — F_4
3561·04	(6)	0·53	0·48	—
3559·53	(6)	0·59	0·58	—
3521·27	(5)	0·51	0·50	D_4 — F_4

(i) Measured shift—long exposure.

(ii) Measured shift—short exposure.

It will be observed that for $\lambda 3521$ the shifts are practically equal, whereas for the stronger lines of this group they are much greater in the long exposure.

The reason for this difference is undoubtedly to be found in the fact that these lines are broadened asymmetrically in the high-pressure spectrum, the intensity falling off more slowly to the red than to the violet. With moderate exposures this does not affect the measured shift, and the different members of a multiplet show approximately the same shift. As the exposure is increased a stage is reached at which the intensity maximum of the shifted line is fully exposed, and increased exposure beyond this results in a gradual movement of the centre of gravity of the line to the red, and it is the centre of gravity which is measured in order to determine the amount of shift.

Photographs with various exposures were taken (long exposures being necessary for the fainter lines), and it is thought that there is no appreciable error on account

of this intensity effect in the list of shifts given. It is also clear why no great difference was observed in the previous spectra, for the intensity was never so great as that of the strong argon lines, and in addition the shifted lines appeared more symmetrical, so that the effect would in any case be smaller.

§ 9. THE TERM SHIFTS IN AII

The term scheme for AII and approximate term values according to de Bruin* are given in figure 4. Nearly forty transitions involving shifts are indicated together with the amount of shift.

Several steady combinations have been included for completeness of description. Some of these have been asterisked to indicate that, although no definite shift was observable on the plates taken, the steadiness of the lines corresponding to these transitions is less certain than in the case of those which are not asterisked. This arises from the fact that the lines concerned occur in the red, or thereabouts, and as no large shifts were observed in this region, it was photographed only under low dispersion, so that a small shift would be less easily detected than in the violet. Moreover owing to the broadening which accompanies the use of a high gas pressure a small shift is on this account alone less evident. It is possible that these lines shift by as much as 0.4 cm.^{-1} , this being about the limit to be placed on their steadiness.

It will be observed that in the quartet system of the main family of terms (3P limit) all transitions other than $4p \rightarrow 4s$ show shifts. The $4p \rightarrow 3d$ transitions show comparatively small shifts, while those from $4d$ and $5s$ terms to a lower state show large shifts. The $5s$ term exhibits a greater shift than the $4d$ terms, and to the probable accuracy of the measurements the three combinations involving the $5s$ term show the same amount of shift. ($4p \ ^4S - 5s \ ^4P$) is represented by only one line for which $d\nu = 6.1 \text{ cm.}^{-1}$. Of the terms arising from the $4d$ configuration $4d \ ^4P$ and $4d \ ^4F$ are affected more or less equally, but $4d \ ^4D$ shows quite definitely a smaller shift than the other two. The lines arising from $4d \ ^4D$ are several in number and there can be little doubt that this lower value is correct.

Only one line belonging to a $6s \rightarrow 4p$ transition has been measured, but the shift of 13.1 cm.^{-1} is much greater than that for the $5s$ term and is not expected to be in error by more than 0.6 cm.^{-1} .

In the doublet system of the main family the shifts are rather smaller than the corresponding ones in the quartet system, but are of the same magnitude. No small shifts have been measured, but as was mentioned above the asterisked zero shifts may in fact be small ones. The doublet combinations corresponding to $3d \ ^4P - 4p \ ^4P$ and $3d \ ^4D - 4p \ ^4D$ are out of range.

For the same configuration of the series electron, the values of the terms based on the 1D state of the core are much smaller than those of the terms based on the 3P state. Thus $3d \ ^2S$ (1D) is actually smaller than $4p \ ^2P$ (3P) and the line $\lambda 4099$, $\{4p \ ^2P_1$ (3P) $- 3d \ ^2S_1$ (1D) $\}$, shows a small shift. Of the combinations involving terms of the 1D family only the $4p \rightarrow 4s$ transitions are steady, as for the 3P family,

* Proc. Acad. Amsterdam, 33, 198 (1930).

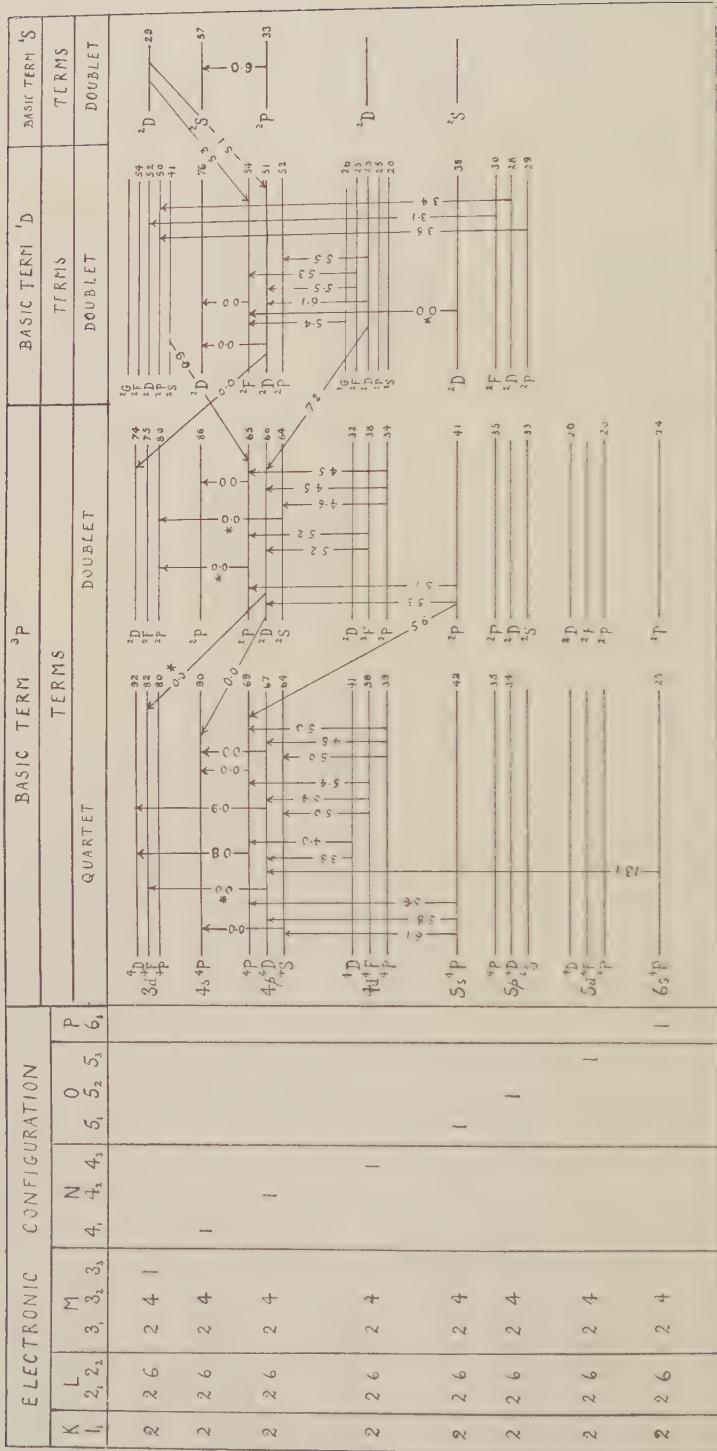


Fig. 4. Combinations and corresponding shifts in AII.

and the $4d \rightarrow 4p$ transitions show rather larger shifts than the corresponding ones in the main family. Several lines which arise from the $5p$ terms have been found to shift. The lower terms in this case are of the configuration $3d$ and the shifts are rather more than half as large as those for the $4d \rightarrow 4p$ transitions.

The lines assigned by de Bruin to a $5s \rightarrow 4p$ transition in the 1D family are steady as far as can be ascertained, and it was at first thought that this was not likely to be the case for such lines, since the $5s \rightarrow 4p$ transitions in the main family showed large shifts. However a consideration of the results for the various spectra indicates that it is probably consistent with the other data. This will be referred to again later.

The observations in the case of the 1S family are very few, but it is of interest to note that here the term values are still smaller than the corresponding ones of the 1D family, and that the $4p\ ^2P(^1D) - 3d\ ^2D(^1S)$ combination shows a large shift. Of the lines arising from $4p\ ^2P(^1S) - 4s\ ^2S(^1S)$ one shows a shift of 6.0 cm.^{-1} , while the other shows apparently only a very small shift. As, however, there is some confusion in the latter case, the former observation has been assumed to represent the behaviour of the doublet.

In all of the transitions so far considered, the lines of any given multiplet have shown the same shift to the limits of accuracy of the observations, provided there is no great intensity difference between the lines. In the case of combinations with $4p\ ^2P(^1D)$ the following were the observed shifts (table 6).

Table 6.

λ	Int.	ν	Classification	$d\nu$
4598.77	(5)	21738.9	$3d\ ^2D_2(^3P) - 4p\ ^2P_2(^1D)$	2.4
4474.77	(6)	22341.3	D_2	5.8
4277.55	(8)	23371.3	$4s\ ^2D_3(^1D) - 4p\ ^2P_2(^1D)$	2.5
4237.23	(7)	23593.7	D_2	2.2
4131.73	(8)	24196.1	D_2	5.0
2979.05	(6)	33557.9	$4s\ ^2P_1(^3P) - 4p\ ^2P_1(^1D)$	4.1
2891.61	(5)	34572.7	P_2	3.9

In addition to the lines of the first two doublets showing different shifts, the lines of the third doublet show shifts which are equal to each other but different from any of the former. It will be noticed that in the first two doublets the shifts associated with $4p\ ^2P_1$ are roughly equal, as are those of the lines assigned to $4p\ ^2P_2$. The terms of this level, $4p\ ^2D$ and $4p\ ^2F$, do not, however, show any shift, and this seems to be the correct behaviour of terms of this level. It is probable therefore that the lines given below have been wrongly classified.

Oxygen group at $\lambda 3217$ and CII doublet at $\lambda 2837$. In addition to the spectra already considered there were observed shifts to the red in a group of three lines in the oxygen spectrum, suggested by Fowler* as being due to OI. The lines and the shifts of two of them are given in table 7.

The third line does not appear to shift.

* Proc. R.S. A, 110, 476 (1926).

Table 7.

λ	Int.	$d\lambda$	$d\nu$
3218·04	(3)	0·48	4·7
3216·74	(2)	0·46	4·5
3216·01	(2)	—	—

The shifts are comparable with those in OII, being measured on the same plates. It will be seen that they are slightly larger than those associated with the $4s$ terms in OII. The spectrum of neutral oxygen, OI, has been much more fully investigated recently, but the above lines do not find a place in the scheme. It is possible that they are connected with a term of the $1S$ family in OII.

A doublet due to singly ionized carbon occurring as impurity in the oxygen spectra also showed a shift to the red (table 8), the displacement being much smaller than in the oxygen groups.

Table 8.

λ	$d\lambda$	$d\nu$	Classification
2837·60	0·10	1·3	$2p' \ ^2S_1 - 3p \ P_1$
2836·71	0·12	1·5	$S_1 - P_2$

Wave-lengths and classifications are by Fowler*. The corresponding doublet in OII has already been considered, the shift being $2·0 \text{ cm.}^{-1}$.

§ 10. COMPARISON OF THE SHIFTS IN DIFFERENT SPECTRA

It was found in the previous work on NII that several factors could affect the amount of shift if the primary exciting conditions were left the same. Hence to compare the shifts in the lines of different spectra it was necessary to ensure that the disturbing forces should be the same for the different atoms, and the best method seemed to be to excite the spectra at the same time in the same tube. It was not possible to produce a photograph with all the spectra considered appearing at once, so that various combinations of two spectra have been investigated. In some cases mixtures in more or less equal proportions of the gases concerned have been employed; in others, the occurrence of air as impurity has been responsible for the nitrogen element.

The following comparisons have been made: (a) Oxygen and nitrogen. The latter was present as impurity. (b) Oxygen and argon. In the first comparison roughly equal proportions of each gas were employed. In the second comparison the argon lines occur as impurity on oxygen plates. (c) Argon and nitrogen. A mixture of the two gases in a ratio of N : A : : 1 : 2 approximately. (d) Neon and nitrogen. Nitrogen lines due to air impurity. (e) Neon and argon. A mixture of the two gases in roughly equal proportions. Only one plate was taken and that not very suitable for measurement.

In this way it has been possible to correlate the term shifts in the various spectra, one assumption being made. It was found in the case of NII, and has been cor-

* Proc. R.S. A, 120, 312 (1928).

reborated in several instances in the present work, that with changed exciting conditions the shifts of the lines are altered in amount, but that they are all changed in the same ratio. This has been assumed to hold for all the spectra in reducing them to a common basis. For simplicity, it has further been arranged to make the comparison taking one term only to represent a particular spectrum.

Thus in (a) the $4s\ 4P$ term in OII is compared directly with the $4s\ 3P$ term in NII. The representative argon term is $5s\ 4P$, but no shifting lines involving this term were observable on the photographs of the mixed gases, so that the comparison in (b) is made by calculation of what the shift in $5s\ 4P$ would be under the conditions yielding the shifts in (i), and comparison of this with the observed shift of $4s\ 4P$ in OII under the same conditions. The results obtained were as shown in table 9.

Table 9.

(a) Oxygen and nitrogen.

λ	NII classification	$d\nu$	λ	OII classification	$d\nu$
3838	$3p\ 3P_2 - 4s\ 3P_2$	4.2	3277	$3p\ 4P_2 - 4s\ 4P_3$	4.1
4227	$3p\ 1P_1 - 4s\ 1P_1$	3.8	3287	$P_3 - P_3$	4.2
			3290	$P_1 - P_2$	4.0
Mean...	4.0			Mean...	4.1

$$\therefore \frac{\text{OII} (4s\ 4P)}{\text{NII} (4s\ 3P)} = \frac{4.1}{4.0} = 1.03.$$

(b) Oxygen and argon.

1st comparison

λ	AII classification	$d\nu$	OII			
		(i)*	(ii)†	(i/ii)	λ	$d\nu$ (i)
3561	$4p\ 2F_4 (1D) - 4d\ 2G_5 (1D)$	3.8	5.1	0.75	3277	5.0
3559	$4p\ 2D_3 (3P) - 4d\ 2F_4 (3P)$	4.4	5.4	0.81	3287	4.5
3545	$4p\ 2F_3 (1D) - 4d\ 2G_4 (1D)$	4.1	5.7	0.72	3290	4.7
Mean ratio...				0.76	Mean...	4.7

Then if $d\nu$ in $5s\ 4P$ in AII (table 4 and figure 4) is taken as 5.7 (adopted mean), under conditions (i) it would be 5.7×0.76 .

$$\therefore \frac{\text{AII} (5s\ 4P)}{\text{OII} (4s\ 4P)} = \frac{5.7 \times 0.76}{4.7} = 0.92.$$

2nd comparison

λ	AII classification	$d\nu$	OII			
		(i)	(ii)	(i/ii)	λ	$d\nu$ (i)
3588	$4p\ 4D_4 (3P) - 4d\ 4F_5 (3P)$	4.2	5.6	0.75	3277	5.0
3576	$D_3 - F_4$	4.2	5.6	0.75	3287	4.5
3561	$4p\ 2F_4 (1D) - 4d\ 2G_5 (1D)$	3.9	5.1	0.76	3290	4.6
3559	$4p\ 2D_3 (3P) - 4d\ 2F_4 (3P)$	4.6	5.4	0.85	Mean...	4.7
Mean ratio...				0.78	Mean...	4.7

$$\therefore \frac{\text{AII} (5s\ 4P)}{\text{OII} (4s\ 4P)} = \frac{5.7 \times 0.78}{4.7} = 0.95.$$

$$\text{Mean of the two comparisons: } \frac{\text{AII} (5s\ 4P)}{\text{OII} (4s\ 4P)} = 0.94.$$

* The values given in column (i) are the shifts measured on the photographs of the mixtures of the various gases.

† The values given in column (ii) are taken from the complete list of argon lines given in table 4.

(c) Argon and nitrogen.

λ	classification	$d\nu$			λ	classification	$d\nu$ (i)
		(i)	(ii)	(i, ii)			
3979	$4p\ ^1S_2(^4P) - 4d\ ^1P_1(^3P)$	3.7	4.9	0.76	3838	$3p\ ^3P_2 - 4s\ ^3P_2$	4.0
3952	$4p\ ^1S_2(^3P) - 4d\ ^3F_2(^1P)$	3.8	5.0	0.76	3830	$P_1 - P_2$	4.0
3946	$4p\ ^2F_4(^1D) - 3d\ ^2D_3(^1S)$	4.1	5.3	0.77			
3932	$4p\ ^4S_2(^3P) - 4d\ ^4P_2(^3P)$	3.4	5.0	0.68	3609	$3p\ ^3S_1 - 4s\ ^3P_1$	4.0
3925	$4p\ ^2F_3(^1D) - 3d\ ^2D_2(^1S)$	4.0	5.2	0.77	3593	$S_1 - P_2$	3.9
3868	$4p\ ^4S_2(^3P) - 4d\ ^4P_3(^3P)$	3.2	5.0	0.64			
3809	$4p\ ^4P_2(^3P) - 5s\ ^4P_3(^3P)$	3.3	5.3	0.62			
		Mean ratio...			3811		
		$\therefore \frac{\text{AII} (5s\ ^4P)}{\text{NII} (4s\ ^3P)} = \frac{5.7 \times 0.71}{4.0} = 1.01.$					

(d) Neon and nitrogen.

NeII	NII			$d\nu$
	λ	classification		
Mean shift for the $4s\ ^4P$ group as given in list of NeII shifts	3838	$3p\ ^3P_2 - 4s\ ^3P_2$	9.3	
	3006	$3p\ ^1D_2 - 4s\ ^1P_1$	9.2	
		Mean...		9.3
		$\therefore \frac{\text{NeII} (4s\ ^4P)}{\text{NII} (4s\ ^3P)} = \frac{7.4}{9.3} = 0.80.$		

(e) Neon and argon.

λ	AII	$d\nu$			λ	NeII	$d\nu$ (i)
		(i)	(ii)	(i, ii)			
3780	$4p\ ^4D_4(^3P) - 4d\ ^4D_4(^3P)$	6.7	4.2	1.60	2792	$3p\ ^4P_3 - 4s\ ^4P_3$	6.7
3476	$4p\ ^4P_3(^3P) - 4d\ ^4D_3(^3P)$	6.5	4.2	1.55			
		Mean ratio...			1.57		
		$\therefore \frac{\text{NeII} (4s\ ^4P)}{\text{AII} (5s\ ^4P)} = \frac{6.7}{1.57 \times 5.7} = 0.75.$					

The ratios are represented, to the accuracy of the determinations, by the following arrangement:

$$\begin{array}{ccccc} \text{OII} & : & \text{NII} & : & \text{AII} \\ (4s\ ^4P) & & (4s\ ^3P) & & (5s\ ^4P) \\ 1.00 & & 0.96 \pm 0.05 & & 0.96 \pm 0.05 \\ \text{or} & & 4.1 & & 3.9 \pm 0.2 \end{array} \quad \begin{array}{ccccc} \text{NeII} & : & \text{OIII*} & : & \text{OIII} \\ (4s\ ^4P) & & (4s\ ^1P) & & (4s\ ^1P) \\ 0.77 \pm 0.04 & & 0.93 \pm 0.05 & & 0.93 \pm 0.05 \\ 3.2 \pm 0.2 & & 3.8 \pm 0.2 & & 3.8 \pm 0.2 \end{array}$$

if we take OII ($4s\ ^4P$) = 4.1 as the basis of the comparison.

In this comparison the following terms have been taken as steady:

$$\begin{array}{ccccc} \text{OII} & \text{NII} & \text{AII} & \text{NeII} & \text{OIII} \\ 3p\ ^4S & 3p\ ^3S & 4p\ ^4P & 3p\ ^4P & 3p\ ^1P \end{array}$$

The calculated values of the ratios are seen to agree very well with the observed:

	OII	AII	AII	NeII	NeII
	NII	NII	OII	NII	AII
Observed	1.03	1.01	0.94
Calculated from the above arrangement	1.04	1.00	0.96

The adopted arrangement seems therefore to be justified, the agreement actually being better than can safely be expected from the measurements. Hence the possible error is given in the comparison as 5 per cent. although in some cases it may be much smaller if a large number of shifts is concerned.

* The ratio of OIII to OII was determined in the investigation of the oxygen plates.

It appears, then, that for the same electron configuration ($4s$) the spectra OII, NII, OIII show very nearly the same shift, while NeII shows about four-fifths of this shift. In AII $5s\ 4P$ is affected to roughly the same extent as the $4s$ terms of the other spectra, and, as the terms of AII are very similar to those of NeII, provided that for a given term of total quantum number n in the latter case we take the term having total quantum number ($n + 1$) in the former, this is what might be expected.

By use of the comparison just made the term values and corresponding shifts for all the terms considered are given in table 10. The terms with zero shift have been adopted as steady. In AII, for the quartet terms of the main family, two sets of shifts are given according to whether the $4p$ terms or the $3d$ terms are assumed steady. The latter (column (ii)) is probably more correct but the former is given because in the other spectra it has been necessary to assume the analogous terms ($3p$) to be steady.

It has been seen that for the $4s$ configuration (in the case of AII the $5s$) the spectra considered all show the effect to more or less the same extent. While a detailed study of the data does not reveal an exact correspondence between the other terms, it is of interest to consider one or two comparisons.

Firstly, the iso-electronic system giving rise to NII and OIII. The term schemes for these two are identical, the difference between the spectra being in the actual term values, which are roughly in the ratio OIII : NII : : 9 : 4; i.e. in the ratio of the squares of the effective nuclear charges. The values are given in table 10.

It will be observed that for three of the four terms for which shift data have been obtained, the term shifts in OIII and NII are roughly equal, but in the remaining case ($4p\ 1D$) the two shifts are considerably different. It may be that the $4p\ 1D$ term in one of the spectra has not been correctly identified.

Secondly, it may be noticed that for successive ionization of the same atom (OII and OIII being the corresponding spectra) the terms corresponding to the same configuration of the series electron are shifted to approximately the same extent. Here, as in the first comparison, the term values OIII : OII are in a ratio of about 2 : 1 if we consider the main family in OII, and considerably more than this if we are concerned with the family having the $1D$ limit. In the third place we may compare the shifts in the spectra of successive members of a column of the periodic table, i.e. NeII and AII. It has been shown by de Bruin* how close is the connexion between the two spectra when the argon term has total quantum number greater by 1 than the neon term with which it is compared. We notice in table 10 that in AII the term value of $5s\ 4P$ is approximately the same as $4d\ 4P$, and similarly, in NeII $4s\ 4P$ is roughly the same as $3d\ 4P$. In the extent to which they shift, however, there is a complete difference, for whereas in AII the terms mentioned show approximately the same shift, in NeII the ratio of the shift of $4s\ 4P$ to that of $3d\ 4P$ is more than three to one. In showing a small shift the $3d$ terms of NeII fall intermediate between the $3d$ terms of OII, NII, and OIII, and the $4d$ terms of AII.

* Proc. Acad. Amsterdam, 31, 593 (1928).

Table 10.

OII							
³ P limit			¹ D limit				
Term	Value (cm. ⁻¹)	d _v (cm. ⁻¹)	Term	Value (cm. ⁻¹)		d _v (cm. ⁻¹)	
2p' ² S ₁	87311	-2.0	—	—	—	—	
3p ² S ₁	79079	0.0	3p ² P ₁	50541	0.0	—	
3p ² P ₁	68851	0.0	—	—	—	—	
3p ² D ₂	71499	0.0	4s ² D ₂	23734	4.0	—	
3p ⁴ S ₂	70859	0.0	—	—	—	—	
3p ⁴ P ₁	74675	0.0	—	—	—	—	
3p ⁴ D ₁	76290	0.0	—	—	—	—	
4s ² P ₁	42692	{ 5.8 4.2	—	—	—	—	
4s ⁴ P ₁	44395	4.1	—	—	—	—	
OIII							
3d ³ F ₃	119935	0.0	3d ³ F ₃	52275	0.0	—	
3d ³ D ₂	117316	0.0	3d ³ D ₂	51384	0.0	—	
3d ³ P ₁	115011	0.0	3d ³ P ₁	49937	0.0	—	
3d ¹ D ₂	111816	0.0	4p ³ S ₁	42254	3.9	—	
4p ³ S ₁	76641	3.4	4p ³ D ₂	35314	3.2	—	
4p ³ D ₂	77999	3.3	4p ³ D ₂	36081	2.8	—	
4s ¹ P ₁	91712?	3.8	4s ¹ P ₁	40987	3.9	—	
4p ¹ D ₁	78870	2.6	4p ¹ D ₂	36153	3.9	—	
NeII							
3p ⁴ P ₁	85033	0.0	4d ³ F ₃	29107	2.8	—	
3p ⁴ D ₁	81791	0.0	4d ³ D ₂	28580	3.9	—	
3p ⁴ S ₂	78678	0.0	4d ³ P	28095	{ 5.5 4.1	—	
3d ⁴ D ₁	52208	0.9	4p ¹ S ₀	36677	1.8	—	
3d ⁴ F ₂	50459	0.9	4d ¹ D ₂	28920	3.7	—	
? 3d ⁴ P ₁	50684	{ 0.8 1.1	5s ³ P ₁	24589	9.2	—	
4s ⁴ P ₁	48951	3.2	5s ¹ P ₁	24019	10.3	—	
AII							
³ P limit			¹ D limit				
Term	Value (cm. ⁻¹)	d _v (i) (cm. ⁻¹)	d _v (ii) (cm. ⁻¹)	Term	Value (cm. ⁻¹)	d _v (cm. ⁻¹)	
3d ⁴ D ₃	92273	-0.6	0.0	4s ² D ₂	76134	0.0	
3d ⁴ F ₄	82037	-0.6	0.0	4p ² F ₃	54354	0.0	
4s ⁴ P ₂	89668	0.0	0.6	4p ² D ₂	51407	0.0	
4p ⁴ P ₂	69403	0.0	0.6	4d ² G ₄	26160	3.1	
4p ⁴ D ₃	67081	0.0	0.6	4d ² F ₃	24520	3.7	
4d ⁴ D ₃	40957	2.7	3.3	4d ² D ₂	25230	4.0	
4d ⁴ F ₄	39130	3.7	4.3	5p ² F ₃	29893	2.1	
4d ⁴ P ₂	38284	3.4	4.0	5p ² D ₂	28133	2.3	
5s ⁴ P ₂	42533	3.9	4.5	5p ² P ₁	28664	2.6	
6s ⁴ P ₂	25617	9.0	9.6				
3d ² D ₂	74280	0.0	—	¹ S limit			
3d ² F ₃	74607	0.0	—	4s ² S ₁	57447	0.0	
4p ² P ₁	65048	0.0	—	3d ² D ₂	28888	3.6	
4p ² D ₃	65361	0.0	—	4p ² P ₁	32421	4.1	
4p ² S ₁	63665	0.0	—				
4d ² F ₃	37165	3.6	—				
4d ² P ₁	34820	3.1	—				
5s ² P ₁	40840	3.6	—				

§ 11. RELATION BETWEEN TERM SHIFT AND TERM VALUE

It has been pointed out that in OII the shift in $4s\ ^2D$ (1D family) is the same as that in $4s\ ^4P$ (3P family), although the values of these terms are quite different. Similarly it has been noticed that in the iso-electronic systems, NII and OIII, corresponding terms show the same amount of shift, although the term values are different. This would suggest that it is the configuration of the series electron that chiefly determines the magnitude of the shifts. In the 1D family of AII, however, the lines assigned to the transition $5s\ ^2D$ to $4p\ ^2F$ are steady, i.e. $5s\ ^2D$ is steady. On the foregoing evidence this was not expected, since the $5s$ terms in the main family are appreciably affected. As the lines concerned are quite strong, and seem to be correctly classified, an attempt was made to see if the results were reconcilable.

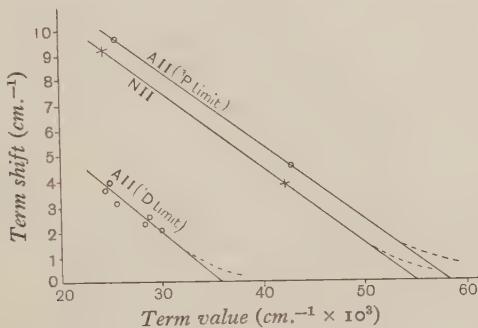


Fig. 5. Relation between term shift and term value.

For the $4s$ and $5s$ triplet terms of NII the term shift was plotted against the term value, figure 5. These were joined by a straight line, and the line was produced to cut the frequency axis. It intersects the latter at about $v 55,000$, which is roughly the value of the terms in NII which are assumed to have zero shifts. The points representing the results for the $5s$ and $6s$ terms of the main family of AII lie very near the NII line, and on production of the line joining these points it intersects the frequency axis at $v 58,000$, at which term value the shift is certainly small, although not quite zero.

If now the observations for the terms of the 1D family of AII are plotted, and the best straight line is drawn through them, it is roughly parallel to the others and cuts the axis at $v 36,000$ approximately, which is less than the term value of $5s\ ^2D$ (1D) ($v 38,000$). That is to say, if we can attach any importance to the approximately linear relationship between term shifts and term values, which is indicated by the results for the main family of AII and for NII, then the deduction is that in the 1D family a term having a value $v 38,000$ should show at any rate a very small if not zero shift, and this is what has been found experimentally.

The probable courses of the curves in the neighbourhood of the axis are shown dotted: it is unlikely that the curves would intersect the axis abruptly. It must be borne in mind that the shift is probably determined only partly by the term value, and the graphical representation indicates only the general behaviour.

A consideration of the inter-combination shifts between the 1D family and the main family suggests that the term shifts for the terms of the 1D family given in table 10 may be low by about $1\cdot0$ cm.⁻¹ in comparison with those in the main family. Any correction on this account would increase all the shifts of the 1D family by the same amount, and would have the effect of shifting the 1D curve in figure 5 parallel to itself, but would not affect the inference drawn with regard to the behaviour of $5s\ 2D\ (^1D)$.

The curves would indicate therefore that there is a more or less regular variation of the term shift with term value. In addition, they show that in the case of AII, for a given term value, the terms of the 1D family are less perturbed than those of the main family, and as the shift appears to be mainly a Stark effect, it means that the 1D family is more stable in the presence of a disturbing electric force than is the main family.

The shifts for terms with the same total quantum number but different azimuthal quantum numbers in NII and AII, when plotted in the above way, do not suggest any regularity between term shift and term value, but it is probable that other factors are responsible for the irregularities.

§ 12. EXAMINATION OF THE SHIFTED LINES WITH A MICROPHOTOMETER

Since the completion of the foregoing work, it has been possible to examine the nature of the lines with a microphotometer (Cambridge Instrument Co.) and the lower part of the plate illustrates some typical intensity curves.

In the first place it will be noticed that the shifted lines are not symmetrical although in the oxygen groups the asymmetry is not very pronounced. The NeII line $\lambda 2809\cdot5$ is likewise fairly symmetrical. $\lambda 6357$ in NII seems rather less symmetrical, and $\lambda 3781$ in AII is still less symmetrical. This line probably represents the least symmetrical of the lines measured.

An endeavour was made in measuring the lines to estimate the centre of gravity of the shifted line, and it seems probable that no appreciable error has been introduced on account of the asymmetry of the shifted lines.

By comparing a photometer record of the low pressure spectrum with a record of the same spectrum under high pressure it can be seen that almost all the broadening is on the long wave-length side. This is seen better in the reproductions of the actual spectra in the upper part of the plate.

§ 13. DISCUSSION OF RESULTS

The displacement of lines associated with the higher terms of a spectrum under certain conditions of excitation has been noticed in several spectra, but it is believed that the present paper and the former one on NII represent the first systematic attempt to investigate the effect, at least as far as the spectra of ionized gases are concerned. The foregoing results show that the "pressure effect" observed first in NII is quite general and affects each of the spectra investigated in much the same

way. K. Asagoe has observed similar shifts in the spectra of chlorine*, bromine and iodine† when excited at relatively high pressures. He did not, however, attempt any correlation of the shifts. More recently‡ he has investigated the Stark effect for many of the lines of these spectra. The results show that the shift caused by raising the pressure of the gas in the discharge tube is in nearly every case of the same type as the Stark displacement.

This strengthens the conclusion arrived at by the author with regard to the shifts in NII, and indicates that although the "pressure effect" is probably not a very pure Stark effect, owing to the variation of the disturbing electric force, it may prove useful in cases where the Stark effect is not determinable in the ordinary way. From the scarcity of Stark effect data for the spectra of ionized gases it seems that these spectra are not easy of investigation by the ordinary methods.

In a recent paper C. J. Humphreys records having observed§ a change of wavelength of many of the arc lines of krypton and xenon when the conditions were such as to excite also the spark spectra, and he attributes the displacement to Stark effect. The lines were under these conditions noticeably diffuse and asymmetrical, with their centres of gravity displaced in the direction of increasing wave-length. With uncondensed discharges, exciting only the spectra of the neutral atoms, the lines are recorded as being exceedingly sharp and perfectly reproducible. This agrees with the present observations on the spectrum of neutral neon.

The spectra of ionized nitrogen, NII and NIII, have quite recently been investigated by K. Asagoe, by the same method that I employed; the chief differences being in the use of air instead of nitrogen, and in the use of higher pressures (7 cm. and 1 atmosphere). As a consequence of the use of these higher pressures his shifts are somewhat larger than those that I ¶ recorded but are otherwise in general agreement. He finds, however, that although for a pressure of 7 cm. his term shifts are all larger than mine in the same ratio (as I had found in my experiments for two different pressures), at a pressure of 1 atmosphere the ratio is different for different terms, being greater for $4s\ 3P$ than for $4p\ 3D$ and $4p\ 3P$. This is important in reducing shifts in different terms to a common basis as has been done in the present paper; but as the pressures and resulting shifts have, in the present case, been kept below the stage at which a departure from the constant ratio has been observed by Asagoe, it is not likely that the adoption of the same reduction factor for all the terms of a spectrum has introduced any error.

In NIII Asagoe finds that lines of the $3p \rightarrow 3s$ transitions show a shift to the violet, but even at the higher of the pressures used the displacements are quite small. No large shifts to the red such as have been observed in NII are recorded. By a consideration of the shifts of some previously unclassified lines in NII it was possible to identify three new singlet terms. The hope was then entertained that

* Mem. Coll. Sci. Kyoto, Univ. A, 10, 15 (1926).

† Jap. Journ. Phys. 4, 85 (1927).

‡ Sci. Pap. Inst. Phys. Chem. Res. Tokyo, 11, 243 (1929).

§ Bur. Standards Journ. Res. 5, 1041 (1930).

¶ Sci. Rep. Phys. Inst. Univ. Tokyo, 1, 47 (1930).

|| In my experiments much larger shifts than those published were obtained but were not considered to be susceptible of sufficiently accurate measurement.

the shift might prove useful in the analysis of spectra. The data for a spectrum of fair complexity, such as AII, although indicating which lines arise from steady and which from perturbed terms, do not assist very much further in the analysis of the spectrum, chiefly owing to the fact that the shifts are so much of the same magnitude. The shifts nevertheless afford a good criterion as to whether the lines assigned to a particular combination are all associated with the same pair of terms.

§ 14. DESCRIPTION OF PLATE

The upper part shows typical shifts in four of the spectra investigated, viz. AII, OII, NeII and NII. In each case there are two spectra in juxtaposition, the low pressure spectrum serving as a standard of reference for detecting the shifted lines. The lower part of the plate comprises microphotometer records of some of the lines investigated. In the OII record, a curve of the high pressure spectrum is arranged above the curve of the same part of the spectrum at low pressure. The vertical lines are drawn in the positions where the maxima of the lower spectrum would occur if the two were superposed. It can be thereby seen which lines are shifted, and the nature of the shift. Below are records of three other shifted lines. In each of the AII and NII records there occurs a steady line which, it will be observed, is practically symmetrical. The faint vertical line in the NeII record is irrelevant.

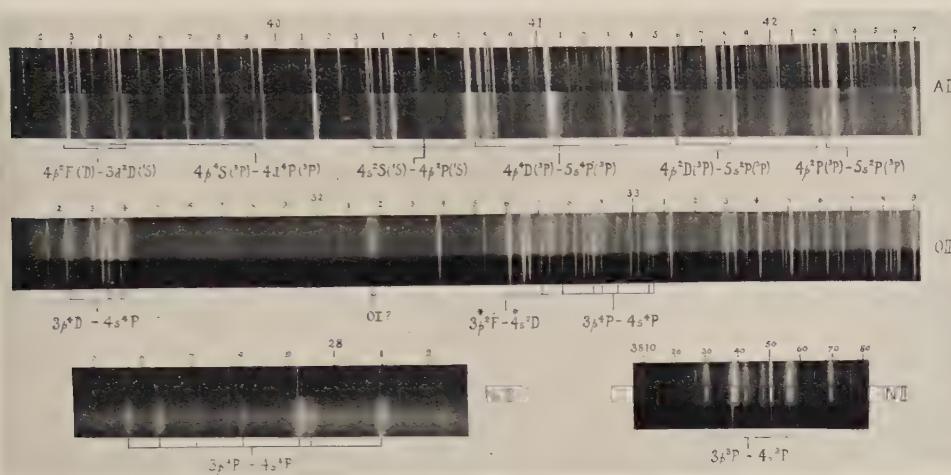
§ 15. ACKNOWLEDGMENT

The author has much pleasure in recording his deep appreciation of the interest which Prof. A. Fowler has shown throughout the investigation.

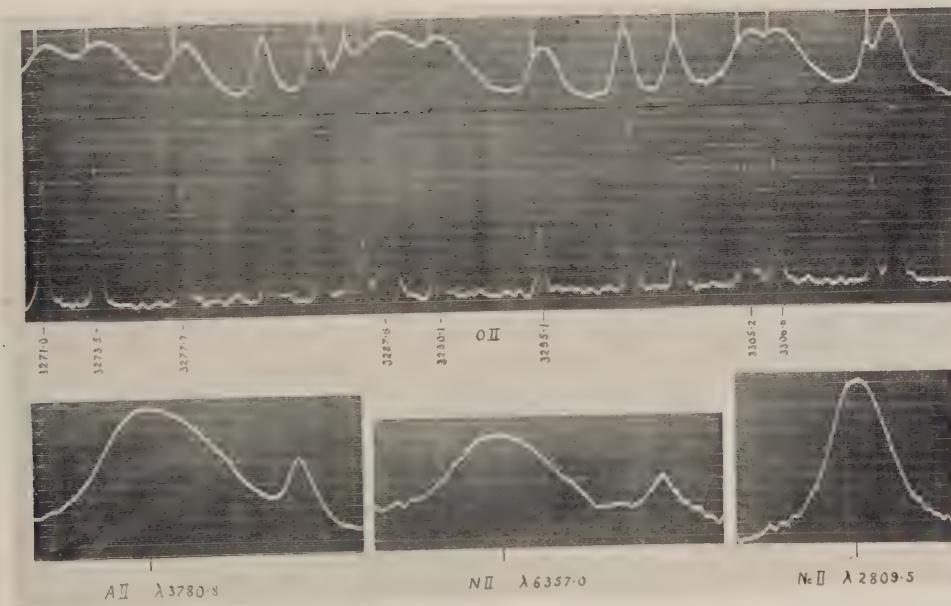
DISCUSSION

MR M. C. JOHNSON. From the point of view of studies of intermolecular forces it is very important that experimental spectroscopists should investigate carefully, as Mr Pretty has done in this paper, the possible distortion of lines by Stark effect. Such work may make possible a decision as to the value of theories of the disturbance of lines by intermolecular fields, such those put forward by Holtsmark and his followers. In comparing those Stark-effect theories with experiment I have generally been forced to conclude that the concentration of free positive and negative charges is too small for the amount by which the line is actually shifted or broadened. Similarly, in the broadened lines of star spectra the Stark effect is qualitatively satisfying but quantitatively inadequate, except perhaps as the modified theory of Stark disturbance suggested by Sir Arthur Eddington in his *Internal Constitution of the Stars*, where he gives reasons for expecting from transitory fields a larger Stark effect than that measured in steady electric fields.

(a)



(b)



PRACTICAL INVESTIGATIONS OF THE EARTH RESISTIVITY METHOD OF GEOPHYSICAL SURVEYING

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ABSTRACT. The paper deals with the methods of geophysical survey which depend on the measurement of the electrical resistivity of the earth. The theory is explained for the case of a single horizontal stratum, and practical tests are described and discussed.

§ 1. INTRODUCTION

GEOPHYSICAL methods have aroused a considerable amount of interest recently in view of the work which has been done all over the world with various types of apparatus. These methods are all based on measurements of variation in some property of the earth such as its density, elasticity, magnetic permeability, and electrical conductivity; some of them have given satisfactory results in the search for mineral bodies. They may be classified as gravimetric, seismic, magnetic and electrical, and the earth resistivity method is one of the simplest of the electrical type. It is the purpose of this paper to explain the theory underlying this method in the simple case of a single horizontal stratum, and to show both theoretically and practically how it can be applied.

§ 2. THE METHOD

The earth resistivity method is based on measurements of the apparent specific resistance of the earth. The presence of any body in the earth, the specific resistance of which differs from that of the surrounding material, will affect the apparent specific resistance to an extent which is dependent on a number of different factors. The method thus affords a means of detecting the presence of such bodies in the earth. Whether the results can be used to determine the exact position of the bodies remains to be seen.

§ 3. THEORY OF THE METHOD

(a) *Fundamental theory.* A method of measuring specific resistance of homogeneous earth is described in a United States Bureau of Standards paper entitled "A Method of Measuring Earth Resistivity" by F. Wenner. Four electrodes are driven into the earth in a straight line at equal intervals a as shown in figure 1,

a

I and a current I amperes is passed between the two outer electrodes, and the potential difference V between the two inner electrodes is measured.

V Then if a is the electrode-interval, and ρ is the specific resistance of the earth,

$$\rho = 2\pi a V/I \quad \dots\dots(1).$$

R If a is expressed in inches, ρ will be given in ohms in.³. If a is in centimetres, ρ will be in ohms/cm.³. The fraction V/I may be termed a resistance and designated R . Then formula (1) may be written

$$\rho = 2\pi a R \quad \dots\dots(2).$$

Since it is only under special conditions that the earth involved in the measurements can be considered homogeneous, the value of ρ obtained by means of these formulae is only an apparent specific resistance, and will be affected by the extent of the non-homogeneity and the electrode separation.

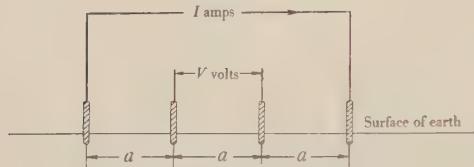


Fig. 1.

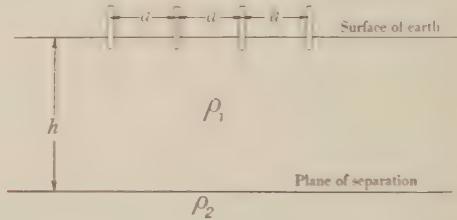


Fig. 2.

(b) *Single horizontal stratum.* One of the simplest cases met with is that of a single horizontal underlying stratum, and the presence of this stratum will affect the value of the apparent specific resistance obtained by the application of equation (2) to an extent which will be dependent on the specific resistance of the surface layer, the specific resistance of the stratum, the depth to the stratum, and the electrode-separation. It is desirable to have some relationship between these various quantities which can be used in such a way that when the values of the apparent specific resistance, the resistance of the surface, and the electrode-interval are known, the depth of the stratum can be calculated. If, as in figure 2, it is assumed that there is a single horizontal stratum at a depth h below the horizontal surface of the earth, that the specific resistance of the surface layer is ρ_1 , and that the specific resistance of the underlying stratum is ρ_2 , it can be shown* that the value of the apparent specific resistance ρ_a , as obtained by the application of equation (2) to the resistance obtained on measurement, is related to the actual specific resistances, depth, and electrode separation by an expression of the form

$$\rho_a/\rho_1 = 1 + 4F \quad \dots\dots(3).$$

F In this expression F is a function representing the sum of an infinite series and may be written

$$F = \sum_{n=1}^{\infty} \left\{ \frac{k^n}{\sqrt{[1 + (2nh/a)^2]}} - \frac{k^n}{\sqrt{[4 + (2nh/a)^2]}} \right\} \quad \dots\dots(4),$$

k in which k has the value,

$$k = (\rho_2 - \rho_1)/(\rho_2 + \rho_1) \quad \dots\dots(5).$$

* E. Lancaster-Jones, *Mining Magazine*, 43, 19 (1930).

In practice ρ_a and a are definitely known, and ρ_1 may be determined by careful measurements with very small electrode-separations, and thus there are two unknown quantities k and h , the latter of which it is desired to ascertain.

It is possible to calculate theoretically the value of the ratio ρ_a/ρ_1 for definite values of k , h , ρ_1 and a . Consider the quantity k equation (5). This may be written as

$$(1 - \rho_1/\rho_2)/(1 + \rho_1/\rho_2)$$

and is therefore dependent only on the ratio ρ_1/ρ_2 . Thus k may have any value between $+1$ and -1 ; the values of ρ_1/ρ_2 corresponding to various values of k are given in table I. Positive values of k correspond with the condition that the lower stratum has the higher resistivity, negative values of k occurring when the resistivity of the lower stratum is less than that of the surface layer.

Table I.

k	ρ_1/ρ_2	k	ρ_1/ρ_2
1.0	1/∞	-1.0	∞
0.9	1/19	-0.9	19
0.8	1/9	-0.8	9
0.7	1/5.67	-0.7	5.67
0.6	1/4	-0.6	4
0.5	1/3	-0.5	3
0.4	1/2.33	-0.4	2.33
0.3	1/1.85	-0.3	1.85
0.2	1/1.5	-0.2	1.5
0.1	1/1.33	-0.1	1.33
0	1/1	0	1

For given values of the electrode-interval a and of k , a curve can be drawn showing the relation between ρ_a/ρ_1 , and h . By giving k the values in table I, a series of curves can be drawn for one given electrode-interval. When k has a positive value, however, it is more convenient to express the results in terms of conductivity by plotting the values of σ_a/σ_1 instead of ρ_a/ρ_1 , σ_a being the apparent conductivity as measured = $1/\rho_a$, and σ_1 the conductivity of the surface layer = $1/\rho_1$. It is obviously as easy to obtain these curves as to obtain those showing ρ_a/ρ_1 since $\sigma_a/\sigma_1 = \rho_1/\rho_a$. Typical curves of these types are shown in figures 3 and 4, which are for electrode-intervals of 150 and 400 ft. respectively. The sets of curves marked A correspond with positive values of k and show the variation of the conductivity ratio σ_a/σ_1 , while those marked B are for negative values of k and show the variation of the resistivity ratio ρ_a/ρ_1 . Similar sets of curves can be drawn for any desired electrode separation.

It is now necessary to devise some means in which the theoretical results can be applied to the values of the apparent specific resistance actually obtained in practice so as to give the values of the depth h .

§ 4. METHOD OF INTERPRETING THE RESULTS

(a) *Empirical method.* The method of interpreting the results that has been used up to the present is an empirical one, and does not appear to be sound as it is not confirmed by any theory. Suppose a series of tests are made at one point, the centre of the electrode-system being kept at that point while the electrode-interval is varied. Then a series of values for the apparent specific resistance ρ_a will be obtained. If a curve of apparent specific resistance against electrode interval be plotted, a sudden change in curvature is taken as indicating the presence of a body which has a conductivity different from that of the surface medium, and it has been assumed that this body lies below the surface at a depth equal to the electrode-interval at which the change in curvature occurs. This interpretation is based on tests carried out by Messrs Gish and Rooney over a filled-in ravine and also on a lake. In the curves representing their observations, they obtained certain changes in curvature at points equal to the depth of the ravine or lake, and concluded from this that the body of earth included in tests of this type is limited substantially in all directions from the line joining the potential electrodes to a distance equal to the electrode-interval.

Most of the users of the method have adopted this way of interpreting their results, but as most of the tests appear to have been carried out in regions where the substructure of the earth was known, they cannot truly be called impartial tests. From theoretical considerations the occurrence of sudden changes of curvature in the curves representing results obtained in the case where there are horizontal strata, over one another, would appear to be unlikely,

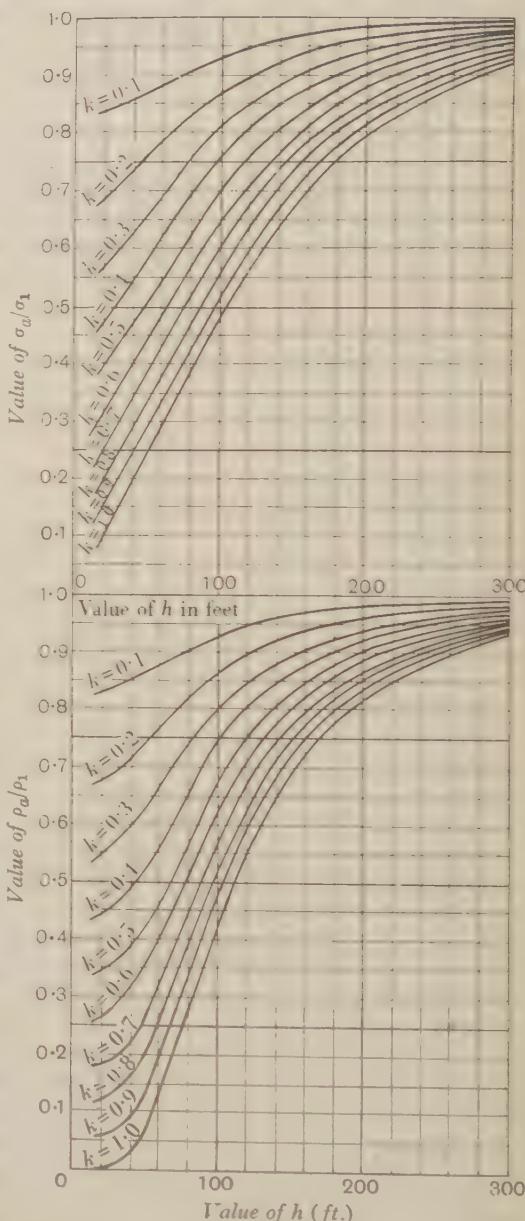


Fig. 3. Curves A 150 (upper) and B 150 (lower).
• Electrode interval 150 ft.

and if it is found, the explanation must be sought in some other type of geological formation.

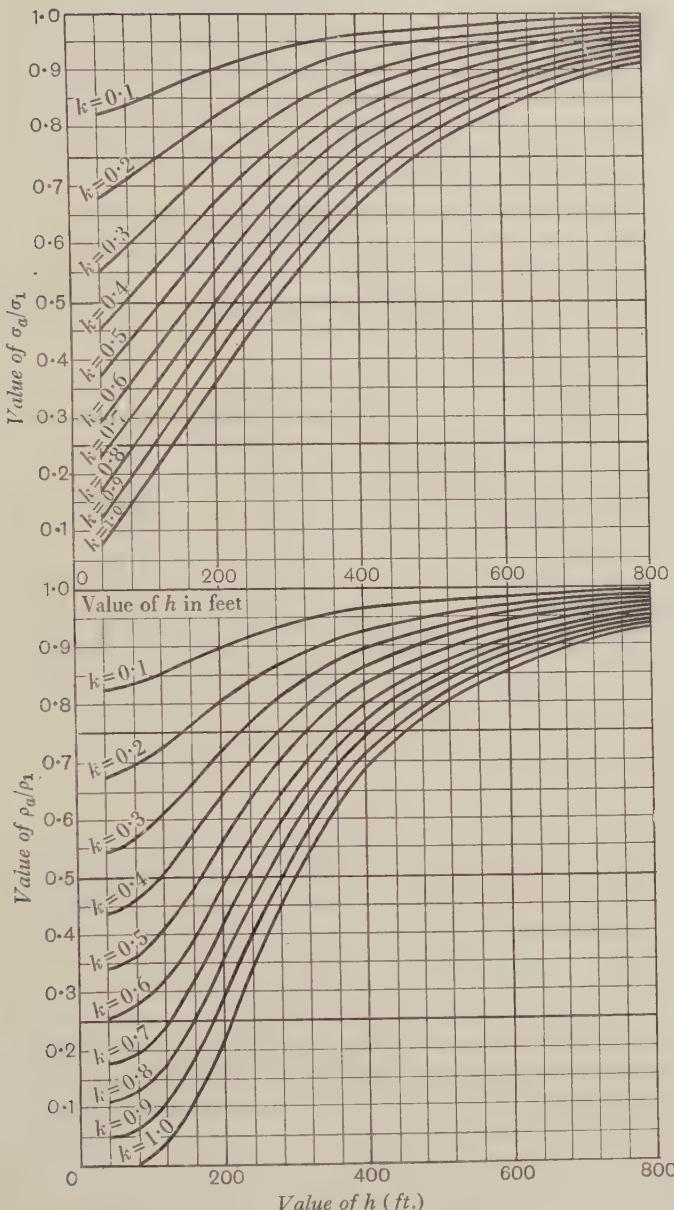


Fig. 4. Curves A 400 (upper) and B 400 (lower). Electrode interval 400 ft.

(b) *Theoretical method.* The author has suggested that the theoretical curves obtained as described above can be used to determine the depth of a horizontal stratum, as follows. Resistivity measurements are first made with one or two small

ρ' , ρ'' , ρ''' electrode intervals, the electrodes in each case being disposed along the traverse in positions symmetrical about the selected station. The object of these first measurements is to enable a fairly accurate determination to be made of the resistivity of the surface stratum ρ_1 . Then further tests are carried out at larger electrode intervals, 150, 200, 250 ft. and so on. In these latter tests the values of the apparent specific resistances are, say ρ' , ρ'' , ρ''' Then the values of the ratio ρ_a/ρ_1 for the various electrode-intervals will be

$$\frac{\rho'}{\rho_1} \cdot \frac{\rho''}{\rho_1} \cdot \frac{\rho'''}{\rho_1} \dots$$

If these ratios are greater than unity ρ_2 is greater than ρ_1 , and the reciprocals of these ratios should be taken. These will be

$$\frac{\sigma'}{\sigma_1}, \frac{\sigma''}{\sigma_1}, \frac{\sigma'''}{\sigma_1}$$

On reference to the curves in figure 3, for an electrode-interval of 150 ft., a series of corresponding values of h and k can be read off, since $\rho_2/\rho_1 = \rho'/\rho_1$ or $\sigma_a/\sigma_1 = \sigma'/\sigma_1$ as the case may be.

Similar sets of values could be read off the curves for the other electrode-intervals. These sets of values can be plotted in curves of h against k . In the theoretically ideal case these curves would all intersect in a point, corresponding to the actual values of h and k . This can hardly be expected in practice, but under conditions corresponding with reasonable approximation to the mathematically ideal case the curves would all intersect within a fairly small area and the centre of this area would give the required value.

§ 5. APPARATUS

There are two forms of apparatus which can be used in carrying out measurements by this method, the first being the potentiometer-milliammeter equipment, originally designed and used by Messrs. Gish and Rooney, and the second, the Megger earth-tester, manufactured by Messrs Evershed and Vignoles, Ltd., London.

(a) *Potentiometer-milliammeter equipment.* The apparatus originally used for the measurement was designed by Messrs Gish and Rooney and employed by them for measurements of the specific resistance of earth in connexion with investigations made for the Department of Terrestrial Magnetism at Washington. It consisted of a potentiometer, milliammeter, battery and set of reversing commutators. A diagram of connexions is given in figure 5. In this figure A is the milliammeter, B the battery, G the galvanometer used with potentiometer, P the potentiometer, C_1 and C_2 the reversing commutators mounted on a common spindle so that the reversals are synchronized.

It was immediately recognized that the employment of direct current would introduce a number of errors such as those due to electrolysis, back e.m.f., and stray currents, and it was necessary to use alternating current in the soil. On the other hand it was more convenient to use direct-current instruments for the actual

measurements, particularly as direct current could be obtained from a portable source such as a battery. It was these considerations which led to the inclusion of the reversing commutator C_1 shown in figure 5, to convert the direct current from the battery to alternating current after it has passed through the milliammeter; and to the inclusion of C_2 to rectify the current produced by the potential difference between the two inner spikes, so that balance can be obtained on the potentiometer.

The use of these commutators introduces a correction-factor into the result if the correct value of R is to be obtained, since the current is definitely switched off for a short period in every half-cycle of the alternating current. The milliammeter reads the current I passing between the outer electrodes, while the potentiometer gives the potential difference V between the two inner spikes. The ratio V/I after modification by the correction-factor caused by the commutators gives the resistance R . An application of equation (2) will then give the apparent specific resistance.

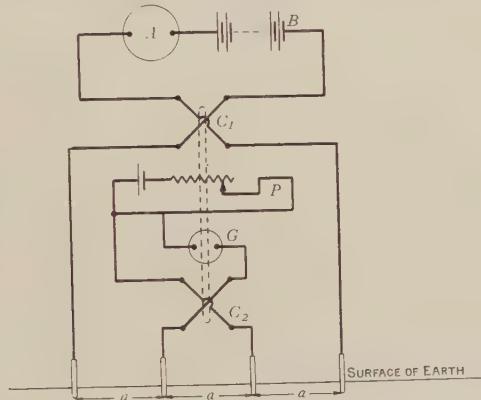


Fig. 5.

The four spikes or electrodes will each have a resistance to earth, and if the ground is dry or sandy these resistances may easily be of the order of several thousands of ohms each. The resistances of the two outer electrodes are included in the main current circuit and reduce the testing current and the voltage drop between the two inner spikes in the same proportion. They do not therefore affect the value of the ratio V/I . If these resistances are so high that they appreciably reduce the current flow, this may be overcome by increase of the battery voltage. The two inner electrodes are connected to the potentiometer, and since no current is taken from them when balance has been obtained, their resistances to earth do not affect the value V measured on the potentiometer. If the resistances of these electrodes are large they may reduce the sensitivity of the potentiometer, but in most cases this will not be serious.

The main drawback to this apparatus is its bulk, as several instruments and a battery are required in addition to the electrodes, connecting cables, etc.

(b) *Megger earth-tester.* The Megger earth-tester is a combined ohmmeter and generator of specialized type, so designed that alternating current is supplied to

the soil section of the testing circuit to overcome difficulties due to electrolytic back e.m.f., and direct current to the measuring part of the testing circuit to allow of the use of the direct-reading moving-coils ohmmeter with its large working force and uniformly divided scale.

The ohmmeter embodies two coils mounted at a fixed angle to one another on a common axle and swinging in the field of a permanent magnet; the axle carries a pointer moving over a scale marked in ohms. A current proportional to the total current flowing in the testing circuit passes through the current coil, while the potential coil carries a current proportional to the potential drop across the resistance under test. The coils are so wound that the resulting forces oppose one another. The final position of the moving coils, and hence that of the pointer, depends on the ratio of the potential drop to the total current, and the instrument is therefore a true ohmmeter giving readings in ohms, which are independent of the applied voltage.

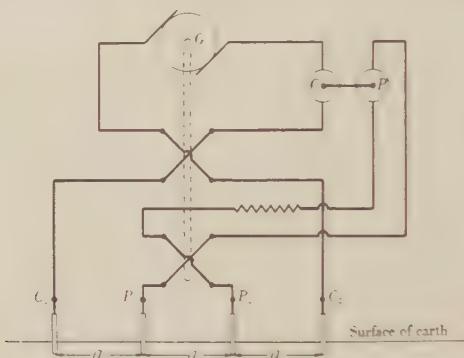


Fig. 6.

The connexions are as shown in figure 6. Direct current from the generator G passes through the current coil C of the ohmmeter to a rotating current-reverser, and to the terminals C_1 and C_2 of the instrument, which are connected to the two outer electrodes. The potential coil P of the ohmmeter obtains its supply from the terminals P_1 and P_2 , which are connected to the two inner electrodes. Since this supply is taken from the soil section of the current circuit, and is therefore alternating, it must be made uni-directional before it passes through the potential coil. A commutator mounted on the same shaft as the main current-reverser, and synchronized with it, is therefore interposed as a rectifier between the terminals P_1 and P_2 and the potential coil. In this manner the current and potential coils of the ohmmeter are both supplied with direct current, and the soil section of the testing circuit is supplied with alternating current.

The instrument is so calibrated that the value of the resistance R in equation (2) is read directly on the scale, so that the apparent specific resistance can be at once determined. The resistances of the outer or current electrodes will not affect the result, for the reason already explained above in connexion with the potentiometer-milliammeter equipment. The resistances of the potential electrodes will, however,

have an effect, as current is taken from them and any large resistances at these points will cause the instrument readings to be too low. In calibrating the instrument a certain value is allowed for the total electrode-resistance and a simple correction can be applied to the resistance obtained to give the correct value. Thus if R_a be the resistance read on scale in specific resistance test, p the total electrode resistance for which allowance is made in calibration, l the total internal resistance of potential circuit of instrument, p_1, p_2 the actual potential electrode resistances, and R the correct value of resistance, then R is given by the formula

$$R = R_a(l + p_1 + p_2)/(l + p) \quad \dots\dots(6).$$

R_a, p
 l
 p_1, p_2
 R

The values of l and p are given on the instruction card supplied with the instrument. The resistances of the potential electrodes may be measured with the instrument itself by connexion of the terminals P_1 and C_1 to one another and to one potential electrode, the second potential electrode being connected to the P_2 terminal, and one of the current electrodes to the C_2 terminal. The instrument then reads the resistance of the electrode directly on the scale. The Megger earth-tester at present used for this class of work has four ranges of 0-3, 0-30, 0-300 and 0-3000 ohms.

In all surveys which have been carried out up to the present time with both the potentiometer-milliammeter equipment and the Megger earth-tester, it has been alleged that there are discrepancies between the values obtained by the two sets of apparatus. Fundamentally there is no reason why the results obtained should not agree.

§ 6. ARRANGEMENTS FOR EXPERIMENTAL SURVEY

(a) *Objects.* In view of the comparatively wide divergence between practice and the results to be expected according to the theory outlined above, and of the need for information on a number of further points, Messrs Evershed and Vignoles, Ltd., instructed the author to carry out an experimental survey using both the Megger earth-tester and a potentiometer-milliammeter equipment. The main objects of the survey were as follows: (i) to test the theory and method described above, (ii) to test the method of interpretation, and (iii) to check the results obtained with the Megger earth-tester against those obtained with the potentiometer-milliammeter equipment.

(b) *Apparatus.* As one of the objects of the survey was to obtain comparative tests of the potentiometer-milliammeter equipment and the Megger earth-tester, it was necessary to take both sets of apparatus. The potentiometer, galvanometer, and standard cell were kindly lent by the Cambridge Instrument Co. Ltd. The milliammeter was made up by Messrs Evershed and Vignoles, Ltd., and had four ranges of 0-100 microamps, 0-1, 0-10, and 0-100 millamps.

The reversing commutators which were used with the potentiometer-milliammeter equipment were similar to those employed in the Megger earth-tester, although they had to be slightly modified before they were found to be completely satisfactory for this type of apparatus. The Megger earth-tester was of the four-range

type mentioned above. A diagram of connexions of the complete equipment is given in figure 7. Various switches were included so that connexions could be changed rapidly from one set of apparatus to the other, and also so that the leads could be reversed and the electrode resistances measured. The apparatus was all mounted on a table and carried in a van.

The electrodes which were used were tubular and were fitted with mild steel caps and driving points. The connecting cables were 4 mm. motor-ignition flexible, and ten coils each of 100 yards were taken. The exact positions of the stations selected for test were obtained by means of compass bearings made on land marks.

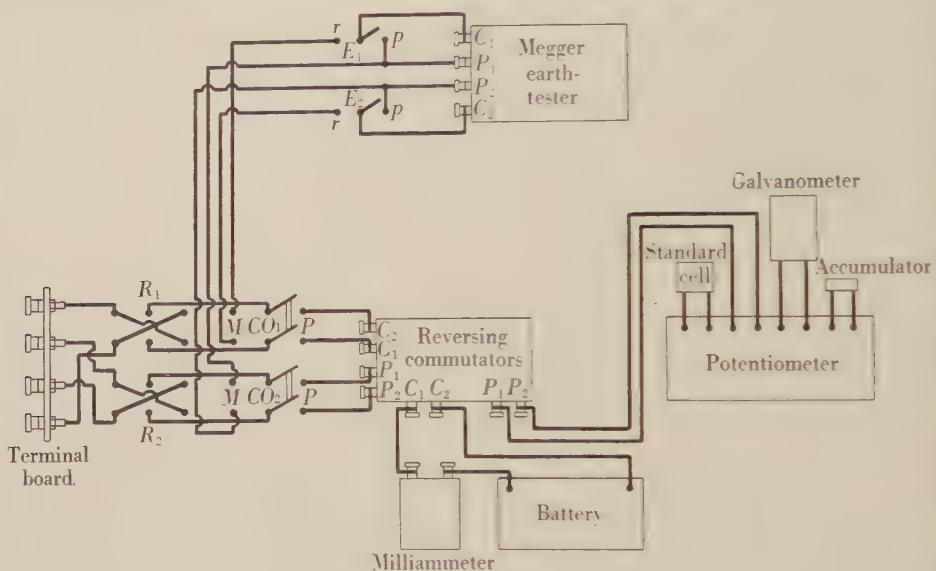


Fig. 7.

(c) *Site.* To investigate the various matters in any satisfactory way it was necessary to obtain a site which would approach as nearly as possible to the ideal case which had been investigated mathematically in the manner indicated above. The Director of the Geological Survey of Great Britain was therefore approached, and asked if he could suggest a site where the surface was approximately level, and where there was an underlying stratum practically horizontal, the electrical resistance being different from that of the surface material. The Director of the Geological Survey went into the matter very thoroughly and suggested a number of suitable sites. The one finally chosen was on Cleeve Hill Common near Cheltenham, Gloucestershire, and permission to carry out the tests was kindly given by the Board of Conservators of Cleeve Common. On the Common, which is in the Cotswolds, the surface material is limestone, the depth varying from 50 to 266 feet. Under this is either sand or clay. On the Common it was found possible to select sites which were practically level and sufficiently large for the tests. The results which were obtained at two stations termed *A* and *B* are given below. At both these stations the ground was practically flat.

§ 7. EXPERIMENTAL RESULTS OF SURVEY

(a) *Station A.* At Station A tests were made with the electrodes on a north-south line only, and results were obtained at electrode-intervals varying from 20 to 500 ft. These results are plotted in the form of curves of the apparent specific

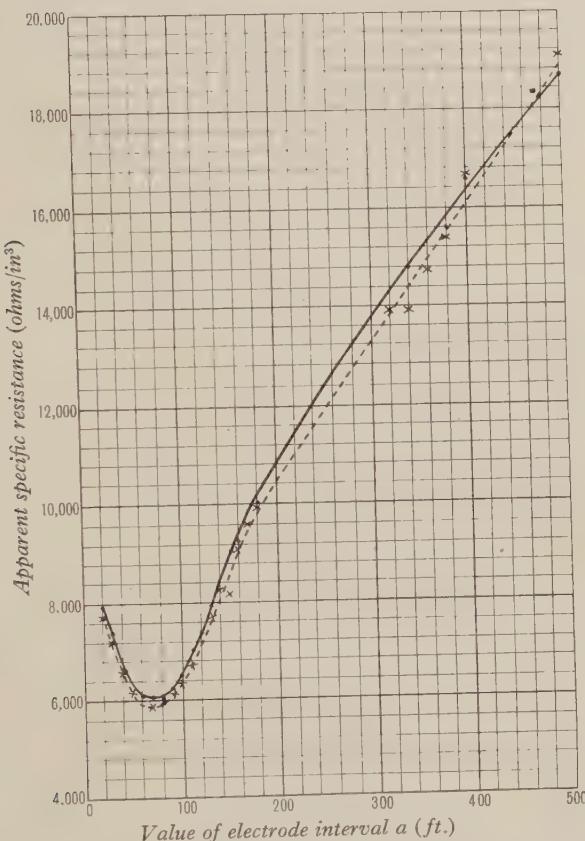


Fig. 8. Station A. Megger earth-tester: experimental points •; curve ———; Potentiometer equipment: experimental points ×; curve - - - - .

resistance against electrode separation in figure 8. The full line represents the results obtained with the Megger earth-tester, and the dotted line those obtained with the potentiometer equipment. It will be noted immediately that the agreement between the two sets of apparatus is very close, and at no point is the difference greater than the possible instrumental and observational errors. Further, with the exception of a dip at the first part of the curve which is due undoubtedly to surface variations, there are no sudden changes in curvature. Although it is known that the depth of the limestone was between 100 and 200 ft., there is no change in curvature at this part of the curve. There is in the apparent specific resistance a steady increase which indicates that the resistance of the underlying stratum is

higher than that of the surface material. To obtain a value for the average specific resistance of the surface material an average of the values obtained at electrode intervals up to 70 ft. has been taken. This average value is 6703 ohms in.³.

Next, from the experimental curve it is necessary to read off the values of the apparent specific resistance at a number of electrode-intervals, and to determine the value of the ratio ρ_a/ρ_1 for each interval. Since the resistance is increasing with the electrode-interval, the ratio ρ_a/ρ_1 will be greater than unity, a fact which indicates that the specific resistance of the underlying stratum is higher than that of the surface material. For the application of the theory outlined earlier the reciprocals of these ratios, namely σ_a/σ_1 must be taken. These ratios are set out in table 2.

Table 2. Station A.

Electrode-separation (ft.)	Apparent specific resistance (ohms in. ³)	Ratio ρ_a/ρ_1	Ratio σ_a/σ_1
150	8,960	1.338	0.748
200	10,740	1.601	0.625
250	12,320	1.840	0.544
300	13,860	2.068	0.483
350	15,220	2.270	0.441
400	16,480	2.460	0.407

With reference now to the theoretical curves worked out for these various electrode-intervals, of which examples are given in figures 3 and 4, a series of values of h and k can be read off for each of the values of σ_a/σ_1 given in this table. The values thus obtained are set out in table 3.

Table 3. Station A.

Value of k	Values of h in feet					
	150 ft. $\sigma_a/\sigma_1 = 0.748$	200 ft. $\sigma_a/\sigma_1 = 0.625$	250 ft. $\sigma_a/\sigma_1 = 0.544$	300 ft. $\sigma_a/\sigma_1 = 0.483$	350 ft. $\sigma_a/\sigma_1 = 0.441$	400 ft. $\sigma_a/\sigma_1 = 0.407$
1.0	180	183	194	204	214	226
0.9	168	170	178	184	193	201
0.8	157	156	161	165	168	173
0.7	144	140	142	142	144	144
0.6	131	124	122	118	116	114
0.5	117	104	98	88	80	67
0.4	99	83	67	45	—	—
0.3	78	51	—	—	—	—
0.2	46	—	—	—	—	—
0.1	—	—	—	—	—	—

Inspection of table 3 shows that the values for $k = 0.7$ agree very closely. The average value of h for this value of k is 142 ft. To obtain the values more closely the figures in table 3 are plotted in the form of curves in figure 9, in which values of h are plotted as abscissae and values of k as ordinates. The six curves intersect in a small area and the centre of the area gives values 142 ft. of h and 0.702 of k . Thus it appears that the depth of the limestone at this point is 142 ft., and so far as it is possible to judge from the geological map this is approximately correct. At this station the method of interpretation suggested by and based upon the theoretical investigation appears to give entirely satisfactory results.

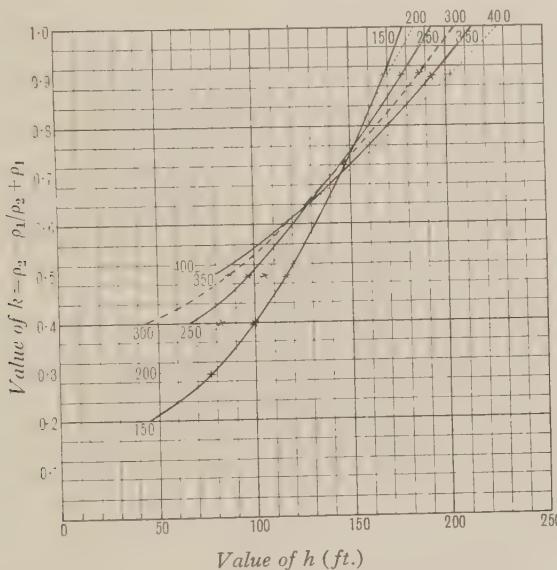


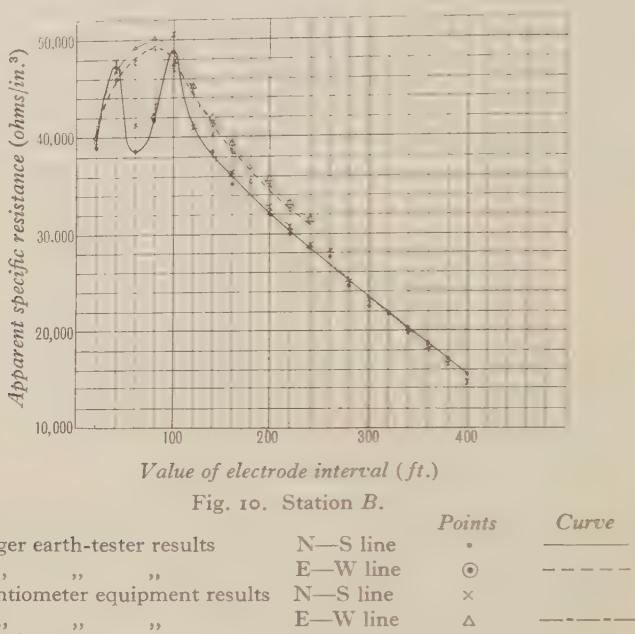
Fig. 9. Station A.

(b) *Station B.* At station *B*, tests were carried out with the electrodes on both the north-south and east-west lines, but while the results obtained on the north-south line are for electrode-separations varying from 20 to 400 ft., those on the east-west line were only obtained for electrode-intervals varying from 20 to 240 ft. The results are all plotted in the form of curves of apparent specific resistance against electrode-interval in figure 10.

It is noticeable that the results on the east-west line appear to be giving a slightly higher value than those on the north-south line. At this station again, as at station *A*, the discrepancy between the Megger earth-tester and the potentiometer-milliammeter equipment is very small, and is again within the limit of observational and experimental errors.

Adopting a similar procedure as for station *A* we obtain the value of ρ_1 as 45,700 ohms/in.³. This value is very much higher than at station *A*, although the surface material is limestone in both cases. The probable explanation of the difference is that at station *A* the stratum under the limestone was clay, which would

keep the limestone waterlogged and thus of a low resistance, while at station *B*, the stratum was sand which would permit water to filter away, leaving the limestone comparatively dry and thus of a higher resistance.

Fig. 10. Station *B*.

	Points	Curve
Megger earth-tester results	•	—
" " "	○	---
Potentiometer equipment results	×	—
" " "	△	---

Table 4. Station *B*.

Electrode separation (ft.)	ρ_a	ρ_a/ρ_1
150	36,800	0.805
200	32,000	0.700
250	27,400	0.600
300	23,000	0.503
350	19,400	0.424
400	15,500	0.339

The experimental curve in this case shows a steady decrease in apparent specific resistance, indicating that the resistance of the underlying stratum is lower than that of the surface material. This condition, again, differs from that at station *A*, where there was a steady increase in resistance and this difference also is due to the presence of clay under the limestone at station *A* and sand at station *B*. With the exception of surface variations at small electrode intervals, there are no sudden changes in curvature. As for station *A*, a series of values of the apparent specific resistance at a number of electrode-intervals was read off the curve and the values of ρ_a/ρ_1 calculated for each. These values are given in table 4. For each of the values

of ρ_a/ρ_1 in the last column, a series of values of h and k was read off from the theoretical curves corresponding to the electrode separation, and the values are given in table 5 and plotted as curves in figure 11. The curve for 400 ft. should

Table 5. Station B.

Value of k	Value of h in feet					
	150 ft. $\rho_a/\rho_1 = .805$	200 ft. $\rho_a/\rho_1 = .700$	250 ft. $\rho_a/\rho_1 = .600$	300 ft. $\rho_a/\rho_1 = .503$	350 ft. $\rho_a/\rho_1 = .424$	400 ft. $\rho_a/\rho_1 = .339$
- 1.0	195	206	218	226	237	240
- 0.9	185	196	206	214	220	219
- 0.8	174.5	184	193	198	200	196
- 0.7	164	172	179	180	185	166
- 0.6	152	158	161	158	150	130
- 0.5	140	142	140	130	112	—
- 0.4	123	121	112	90	—	—
- 0.3	103	94	70	—	—	—
- 0.2	74	44	—	—	—	—
- 0.1	—	—	—	—	—	—

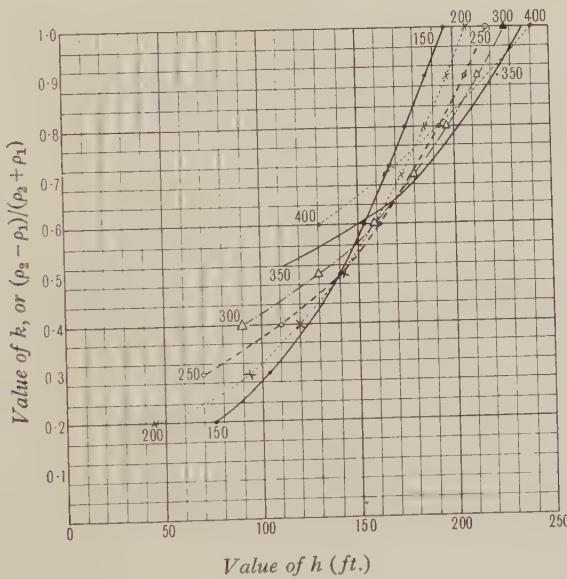


Fig. 11. Station B.

really be ignored, as at a distance of about 500 ft. from the station the ground was beginning to slope in a northward direction. The centre of the area of intersection of the remaining curves gives values of 156 ft. for h and - 0.6 for k . The value of h again agrees closely with that estimated from the geological map. Thus the method of interpretation based on the theory seems again to give entirely satisfactory results.

§8. CONCLUSIONS

From the results of the tests the following conclusions can be drawn:

(i) There is no fundamental disagreement between the values of resistance obtained by the use of the Megger earth-tester and of the potentiometer equipment. Such differences as occur do not exceed 5 per cent. except in very isolated cases and can reasonably be attributed to instrumental errors. One item which contributes to this instrumental error is the error in the correction-factor for the commutators, which cannot be considered to be less than 3 per cent. There is of course no theoretical reason for expecting any difference between the values obtained with the two sets of apparatus.

(ii) In the curves of experimental results there are no sudden changes in curvature, with the exception, of course, of those due to the surface variations. This seems to confirm the theory, and also to discredit the method of interpretation which relies on the appearance of sudden changes in curvature in the curves.

(iii) The application to the experimental results obtained at stations *A* and *B* of the method of interpretation based on the theory worked out above gives satisfactory results. There does not appear to be any reason why perfectly satisfactory theories should not be developed for various cases of earth structure, and methods of interpretation evolved which are based on these theories. The author is proceeding with the investigation of a rather more complicated type of earth structure with a view to developing further methods of interpretation analogous to that described above.

§9. ACKNOWLEDGMENT

The author's thanks are due to Messrs Evershed and Vignoles, Ltd., under whose auspices the experimental survey was carried out, and for their permission to publish the information contained in this paper.

DISCUSSION

Prof. A. O. RANKINE. Mr Tagg has presented this paper in a very clear way. I am glad that the Physical Society has decided to publish this paper belonging to the field of applied geophysics, and hope that it will continue to provide a channel of publication for similar papers of sufficient merit. It was in 1923, I think, that the Society published two important papers by Mr Lancaster Jones and Capt. Shaw on the use of the Eötvös torsion balance, and it has been interesting to note that there have since been many demands from all over the world for the particular part of the *Proceedings* containing them. I am not suggesting increase of sales as the main reason why papers should be accepted. In respect of contributions on practical geophysics it is rather a question of securing that they should become subject to criticism by physicists, and not escape it by being presented to a geological or mining society or journal.

Mr J. H. AWBERY. In reducing the results of the observations, it is necessary to divide each of the quantities ρ' , ρ'' ... by ρ_1 , the surface resistivity. Mr Tagg states that this was obtained by averaging the apparent resistivities to an electrode separation of 70 ft. Can he state the effect of taking some other estimate for ρ_1 , and, in particular, is it possible that some process of successive approximation could be used to improve the final accuracy? In other words, if it had been found that the surface stratum extended downwards to about 142 ft., would there be an advantage in selecting some electrode distance related to this figure, and carrying the calculation through afresh? In the second place, I would ask for the values of ρ_2 found at the two stations. We have k in each case, which gives ρ_1/ρ_2 for each station, but it would be interesting to show ρ_2 explicitly, having regard to the value of the underlying stratum. I should also like to associate myself with Prof. Rankine's remarks on the value to the Physical Society of papers on applied physics. These can be quite as scientific, in the true sense, as papers on pure physics.

Mr T. SMITH remarked that the observer had to start from an assumed value of the depth, and in general this would be a wrong value. Was it possible to find any criterion for determining the sign of the error, and so ensuring a move in the right direction at the next trial?

Mr S. WHITEHEAD. I should like to ask the author whether he could give a rough estimate of the greatest depth of the plane of separation for fairly accurate results, presuming the lower stratum to have a resistivity some few times that of the upper, which is assumed of the order of 10,000 ohms/cm. or less. The method described would be of great value in surveying the electrical properties of the ground with a view to application to the linear flow of alternating current therein. When alternating current flows along a conductor such as an overhead line or cable and returns through the earth, the e.m.f. in the earth near the conductor does not vary very greatly with resistivity, but in regions remote from the conductor the e.m.f. varies rapidly with resistivity. This problem is of considerable practical importance and has been studied for some years by international committees (the C.C.I. and C.M.I.). The results of experiments in Germany, Sweden and America on the distribution of a linear flow of alternating current have not shown correlation with continuous-current tests or tests employing apparatus similar to the author's, where skin effect is neglected and the current distribution is similar to that for a continuous current. In some English tests some degree of correlation was observed, the conditions being more advantageous. The discrepancies appear to have been due to an incomplete interpretation of results so that only resistivities near the surface were obtained, which were not important in the linear flow tests. Since only a few linear flow tests (in which the distribution of current over a wide tract is observed) can be carried out, owing to labour and expense, it would be of great value if tests such as the author's could be used to determine the resistivities of different layers to a sufficient depth. If this were possible without inconveniently increasing the depth of the probes or the separation of the electrodes, then the

linear flow distribution at different frequencies could be deduced, special tests being avoided, while those made could then be interpreted more scientifically.

AUTHOR's reply. Before replying to the various comments which have been made on my paper I should like to thank the Physical Society for accepting it, and I quite agree with Prof. Rankine that papers of this type should be criticized, if necessary very severely, by physicists.

Mr Awbery asks what would be the effect of taking some value for ρ_1 other than that which was obtained by averaging the first part of the experimental curves. If an incorrect value were taken, the area of intersection of the final curves would be very considerably increased. I do not think that a process of successive approximation would be of any use in improving the final accuracy. There is no definite relation between any electrode separation and the depth of the stratum, since the effect of the underlying stratum on the result obtained for any given electrode separation will depend not only on the depth of the stratum but on its resistivity as compared with that of the surface layer.

The values of ρ_2 can be obtained from the values of k , obtained experimentally, table 1, and the values of ρ_1 . Thus at station A, k is equal to 0.7 and from table 1 this gives a value for ρ_1/ρ_2 of 1/5.67. The value of ρ_1 is 6700, and thus ρ_2 will be 38,000 ohms/in.³.

Again, at station B the value of k is -0.6, and this corresponds to a value for ρ_1/ρ_2 of 4. As ρ_1 is 45,700 ohms per inch cube, this means that ρ_2 is 11,925 ohms per inch cube.

In reply to Mr T. Smith I would mention that the observer does not start from an assumed value of the depth. This is one of the main points in favour of the method. The observer is totally unaware of the correct depth and deduces his result by a mathematical process. There is no criterion for giving an algebraic sign of the error.

Mr S. Whitehead's remarks are very interesting, and I would first of all mention that the maximum depth of the plane of separation for accurate results depends only on the sensitivity of the apparatus which is employed. The greater the depth of this plane of separation, the greater must be the maximum electrode separation used, in order to obtain accurate results. The greater the electrode separation, the lower will be the resistance measured, thus necessitating the use of more sensitive apparatus. In the case of the experimental survey described in the paper, the maximum electrode separation used was 500 ft., and at this value the resistance measured was about 0.5 ohm, but we had high-resistance soil either at the surface or in the underlying stratum keeping the resistance up. We could, with the apparatus at our disposal, have worked to a depth of about 500 ft. More sensitive apparatus is being developed so that greater depths can be employed.

I am very interested in the application of resistivity methods which is described by Mr Whitehead and I agree that the method I described could be used. I have read a report which introduces this method of earth resistivity in connexion with the impedance of overhead power lines, and I thought at the time that an independent determination of the earth resistivity would be of assistance. I believe that in-

dependent measurements were made in a method similar to the one I have described, but the results were taken as giving the surface resistivity and the effects of underlying strata were ignored.

Another point which must be borne in mind is that if tests are carried out at high frequencies, errors will be introduced in the result owing partly to the inductance of the earth and partly to the effect of inductance and capacity between the connecting leads. All our tests were carried out at $50\sim$, and a variation of the frequency between 20 and $80\sim$ did not produce any effect on the results. I believe that the skin effect mentioned by Mr Whitehead is due to the presence of the overhead conductor and so could not be taken into account in any independent resistivity tests.

With regard to the question of several layers, the method I have described might be useful for giving average resistivities of some kind, but the actual interpretation in terms of depth and resistivities would be a very difficult one. The theory of multilayers has been worked out by Dr Hummel of Göttingen University*, but the result is very complicated. No method has been devised whereby this very complex theory could be applied to practical tests.

* See *Zeitschrift für Geophysik*, 5, Nos. 5 and 6 (1929).

A PHOTOELECTRIC SPECTROPHOTOMETER FOR MEASURING THE AMOUNT OF ATMOSPHERIC OZONE

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ABSTRACT. A special instrument is described in detail which has been designed in order to allow measurements of the amount of ozone in the atmosphere to be made easily and rapidly under nearly all conditions. The instrument follows the usual practice of measuring the absorption by the ozone of solar ultra-violet energy; from this measurement the amount of ozone can be deduced. A double quartz monochromator isolates certain pairs of wave-lengths, and the relative energy in the two wave-lengths of a pair is measured by allowing them to fall alternately on to a photoelectric cell, the current from which is amplified by thermionic valves. This allows great sensitivity to be obtained so that very small amounts of light can be accurately measured. For measuring the amount of ozone a pair of wave-lengths, one of which is strongly absorbed by ozone while the other is not, is selected. It is shown how the amount of ozone can still be measured when the sky is cloudy if a second pair of wave-lengths, both unabsorbed by ozone, be also measured. The results of tests which show that the accuracy is ample for meteorological requirements are given.

§ I. INTRODUCTION

ONE of the most interesting results which was obtained from the early measurements* of the amount of ozone in the atmosphere was the close connexion which was found between the amount of ozone and the type of atmospheric pressure-distribution. An attempt was made to study this relationship in N.W. Europe during 1926–27†, and six special spectrographs were built for the purpose and distributed to stations scattered over that area. With these instruments spectra were taken of direct sunlight, from which the amount of ozone could be calculated, the plates being returned to be developed and measured at Oxford. While much useful information was gathered from this series of observations, it was naturally found that the delay caused by the return and measurement of the plates, and especially the fact that no observations could be made on cloudy days, were very serious disadvantages. Some of the most interesting meteorological conditions are always associated with much cloud, so that it was very difficult to get any ozone measurements in these cases. As it seems possible that fuller knowledge of the connexion between the amount of ozone and the pressure-distribution might lead to a better understanding of the nature and behaviour of cyclones and anticyclones, it seemed very desirable to design an instrument which should give direct readings

* *Proc. R.S. A*, 110, 660 (1926).

† *Proc. R.S. A*, 114, 521 (1927); 122, 456 (1929). The distribution of ozone over the world is discussed in *Proc. R.S. A*, 129, 411 (1930).

of the amount of ozone without the use of a photographic plate and which could be used even when the light was very weak, so that observations could be taken when the sun was low or by using the light which had passed through clouds. This latter requisite involves difficulties other than the strength of the light available; these will be dealt with later. A very brief sketch of the instrument and the principle involved was given at the Society's Discussion on Photoelectric Cells, but as the instrument has now been in regular use for several months and has proved very satisfactory, it may be useful to give a detailed account of it.

§ 2. GENERAL PRINCIPLE

By means of a double quartz spectroscope, two narrow bands in the ultra-violet region are isolated. The wave-lengths of these bands are chosen so that the longer one is almost outside the great ozone absorption band in the region 3200 Å.U. to 2200 Å.U., while the shorter one is well within it. By measuring the ratios of the energies received from the sun in these two bands, and knowing certain constants

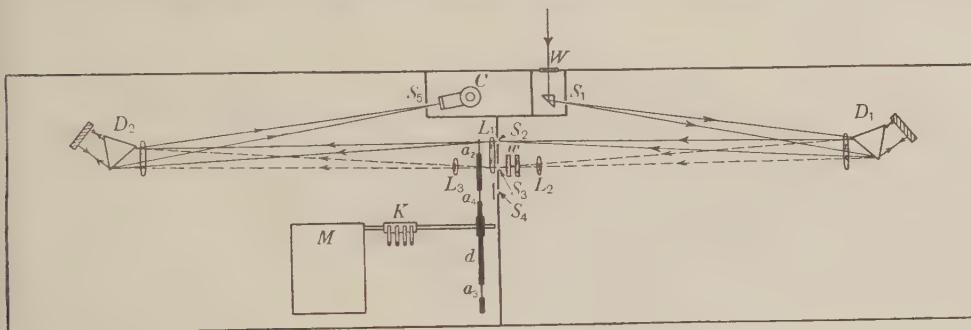


Fig. 1.

which will be discussed later, we can calculate the amount of ozone through which the sunlight has passed. To determine this ratio the two wave-lengths are allowed to fall alternately, by means of a rotating sector wheel, on to a sodium photoelectric cell. The strength of the brighter beam (that of longer wave-length) can be reduced in a known ratio by an adjustable optical wedge. The cell is connected to the first grid of a four-stage low-frequency valve amplifier, figure 3. With such an arrangement only fluctuations in the current are amplified, and if it should happen that the current passed by the cell was exactly the same whichever wave-length was falling on it, then the steady current so produced would not be amplified and there would be no current in the output circuit. The optical wedge is adjusted so that this condition is obtained, and the position of the wedge then allows the ratio of the intensities of the two wave-lengths to be read off when certain constants of the instrument are known. It will be seen that the total intensity of the light does not affect the setting of the wedge, which is determined by the ratio of the intensities only; this is a most important condition since the total light may fluctuate greatly in a short time owing to varying thickness of cloud etc. while the ratio of the intensities of the wave-lengths remains constant.

An alternating-current instrument might be used to read the current flowing in the output circuit, or this current might be rectified by a valve or metal rectifier and a direct-current instrument employed. There are, however, several objections to either course. In the first place, with the high amplification used there must be valve-noise currents in the output circuit amounting to a few μA , so that if rectifiers are used the current can never be reduced to zero for any setting of the optical wedge; also any vibration of the instrument will increase this current owing to microphonic effects, so that its minimum value will not be constant. Secondly, alternating-current instruments are generally less sensitive than direct-current instruments, and if rectifiers are used they are apt to have approximately square-law characteristics for very small currents, so that they are unsuitable for showing

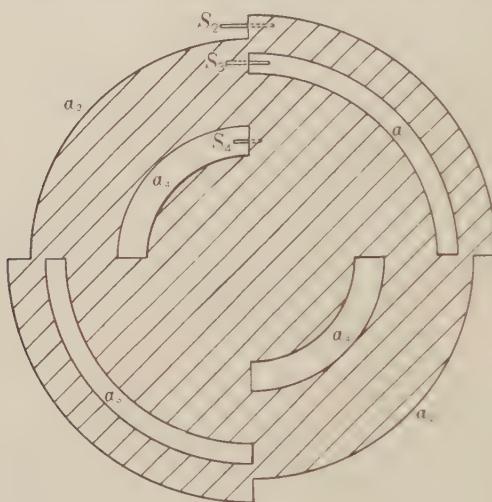


Fig. 2.

when the current is zero within a few hundredths of a microampere. In the actual method used there is mounted on the shaft carrying the sector wheel a commutator which reverses the direction of the current in the output circuit at the right times, thus converting the alternating current into a pulsating unidirectional current which is read on a d.c. microammeter. The strength of this current is directly proportional to the difference in intensity between the two beams, and is in one direction if one beam be the stronger and in the other direction if the other beam be the stronger. This is most important for quick and accurate setting of the wedge.

There is one serious disadvantage of using a commutator with an amplifier giving such large amplification as that used here, since, owing to the fact that the output circuit must be either broken or short-circuited at each reversal, a disturbance is set up and in some way which we have not yet been able to ascertain causes the galvanometer to be rather unsteady. This makes it difficult to tell when the current is exactly zero unless a very heavily damped galvanometer be used which makes observation slow. At the Discussion on Photoelectric Cells, I suggested that

if instead of an ordinary commutator, one on the principle shown in figure 4 were used, there would never be any break or short-circuit, and the unsteadiness might be greatly reduced. In practice the commutator is made by taking a dynamo commutator with about 50 segments and connecting adjacent segments together by a suitable resistance. Two segments at the opposite ends of a diameter are connected to two slip-rings through which the current from the amplifier is led in. It has not

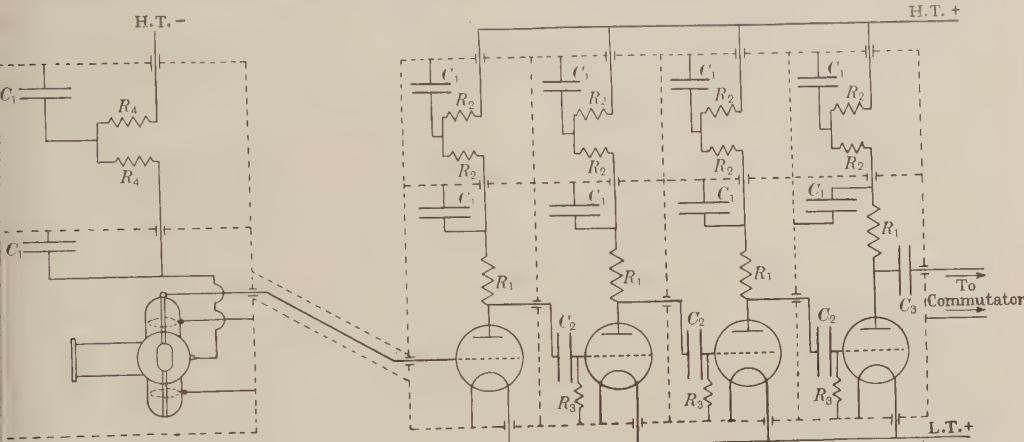


Fig. 3. Electrical system. Broken lines indicate screening.

$C_1 = 2\mu F$; $C_2 = 0.01\mu F$; $C_3 = 2\mu F$; $R_1 = 0.1 M\Omega$; $R_2 = 0.005 M\Omega$; $R_3 = 5 M\Omega$; $R_4 = 0.1 M\Omega$.

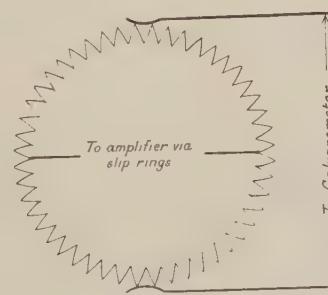


Fig. 4.

yet been possible to fit such a commutator to the spectrophotometer, but tests made by Dr Perfect and Mr Thomas at the National Physical Laboratory on photoelectric measurements with an amplifier similar to that used here show that the unsteadiness is much reduced. The chief effect of fitting such a commutator to the instrument will be to allow readings to be taken more quickly, while observations made when there is little light available will be materially improved in accuracy, so that measurements may be made when the sun is somewhat lower than the altitudes which at present permit of observations.

The amount of amplification that can usefully be employed is fixed by the unsteadiness referred to above and the galvanometer which it is convenient to use.

When the amplification is so great that the pointer becomes markedly unsteady, further amplification is useless. We have worked with a microammeter which was somewhat heavily damped, reading $6 \mu\text{A}$ for a full-scale deflection, and with this the four-valve amplifier is all that is wanted. Direct measurements show that the current amplification obtained is about 10^8 .

Since the intensity of daylight in the region of 3110 \AA.U. , where the measurements are made, is very small compared to that in the longer wave-lengths, if a single spectroscope were used the light of longer wave-lengths which was scattered by the lens and prism surfaces would be an appreciable part of that falling on the photoelectric cell. For this reason a double spectroscope must be used, so that this scattered light is again dispersed and a negligible amount falls on the cell. The general arrangement of the instrument is seen in figure 1, and the relative positions of the slits and the sector-wheel in figure 2. The radiation passes into the instrument through a window W to the first slit S_1 and thence to the first dispersing system D_1 . Three slits S_2 , S_3 , S_4 isolate three narrow bands at 3110 \AA.U. , 3265 \AA.U. and 4435 \AA.U. (S_4 is for measuring the transparency of the atmosphere for wave-lengths unaffected by ozone as described below). The dispersing system D_2 is similar to D_1 , and recombines on slit S_5 radiations of the proper wave-lengths which have passed through S_2 , S_3 and S_4 , but disperses radiation of other wave-lengths which may have passed these slits, so that it will not fall on S_5 . Two narrow optical wedges α of neutral gelatine between quartz plates serve to reduce by an accurately known amount the intensity of the radiation which has passed S_5 . Immediately behind S_5 is the sodium photoelectric cell C . The sector-wheel d revolves close to S_2 , S_3 and S_4 and admits light from S_2 and S_3 alternately (or from S_3 and S_4 if required). K is the commutator and M the driving motor.

§ 3. THEORETICAL BASIS

As was stated before, the instrument was designed to work with either the direct light from the sun, the light from the blue sky overhead or the light from a thinly clouded sky overhead. Each of these conditions must be considered separately and for simplicity the following notation will be used throughout:

x

x is the equivalent vertical thickness in cm. of the ozone present in the atmosphere reduced to a layer of pure gas at 0° C. and 760 mm. of mercury;

a, a'

a, a' the absorption coefficients of ozone per cm. of pure gas at 0° C. and 760 mm. for the wave-lengths 3110 \AA.U. and 3265 \AA.U. ($a = 1.275$, $a' = 0.122$);

I_0, I'_0, I''_0

I_0, I'_0, I''_0 the intensities of the wave-lengths 3110 \AA.U. , 3265 \AA.U. and 4435 \AA.U. as received from the sun on the outside of the atmosphere;

I, I', I''

I, I', I'' the intensities of the same wave-lengths as received at the earth's surface;

K

K the constant of the optical wedge used for the wave-length 3265 \AA.U. ;

Z

Z the apparent zenith distance of the sun at the place of observation;

ζ

ζ the zenith distance of the sun at the place where the sun's ray which reaches the observer cuts the ozone layer; and

β, β', β''

β, β', β'' the extinction coefficients of the atmosphere due to scattering by pure

air and small particles, for the wave-lengths 3110 Å., 3265 Å. and 4435 Å. respectively. (For average conditions at Oxford $\beta = 0.44$, $\beta' = 0.36$, $\beta'' = 0.11$.)

(a) Measurements with direct sunlight. We have shown* that the amount of ozone in the atmosphere is related by the formula

$$x = \{\log(I_0/I'_0) - \log(I/I') - (\beta - \beta') \sec Z\} / (\alpha - \alpha') \sec \zeta$$

to the intensity of direct sunlight received at the earth's surface. The value of $\log(I_0/I'_0)$, and similarly of $\log(I'_0/I''_0)$, can be found from a series of observations

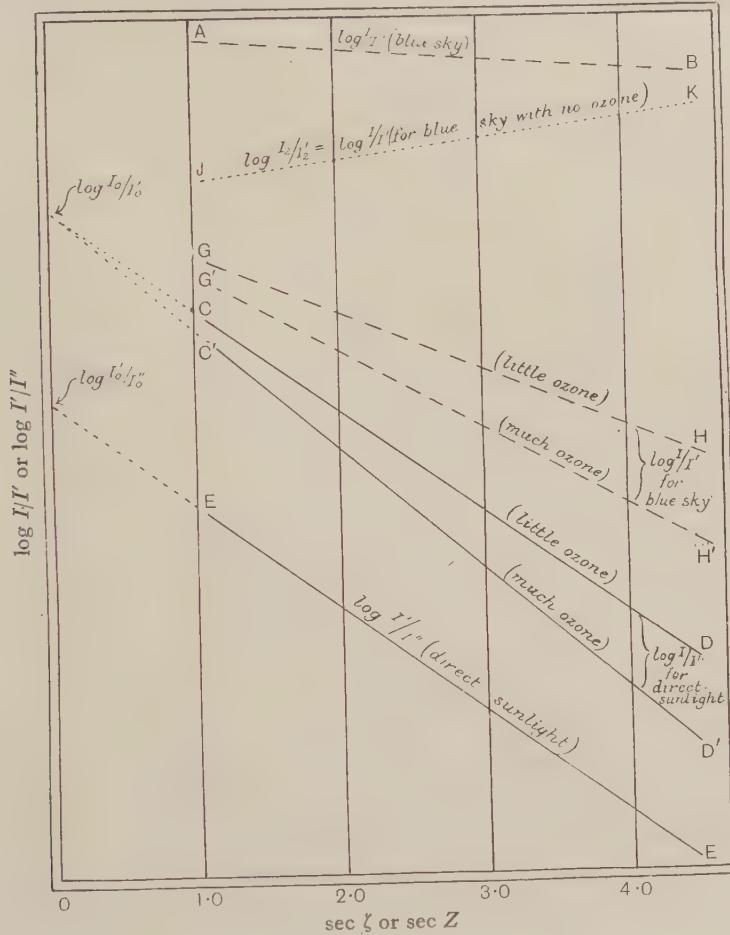


Fig. 5.

extending throughout the day, and having different values of $\sec \zeta$, or $\sec Z$, when the atmospheric conditions are remaining uniform. Since $\log(I/I')$ is a linear function of $\sec \zeta$ †, the observed values of $\log(I/I')$ should lie on a straight line when plotted against $\sec \zeta$ (see CD , figure 5), and by extrapolation of this line the value of $\log(I_0/I'_0)$ may be found. The value of $\log(I'_0/I''_0)$ is found in a similar way.

* Proc. R.S. A, 110, 668 (1926).

† See § 5 for details.

The value of $(\beta - \beta')$ will depend on the clearness of the atmosphere, but the variations will generally be small since the wave-lengths have been chosen as near together as other circumstances will permit. In our older, photographic measurements this value was assumed to remain constant and it was known that a very small error must result. In the new photoelectric instrument $\log(I' I'')$ is measured also and since the corresponding wave-lengths are outside the ozone absorption band* this allows us to determine $(\beta' - \beta'')$ when we have found the value of $\log(I_0' I_0'')$, which we assume to remain constant. We can calculate the value of $(\beta - \beta')$ from $(\beta' - \beta'')$ if we know how β varies with the wave-length. Two formulae for this have been proposed. Formula (1) supposes that the scattering may be treated as made up of two parts, one due to particles which are large compared to the wave-length and which therefore scatter all wave-lengths alike, and one due to air molecules and small particles which scatter according to the inverse-fourth power of the wave-length. (2) The second formula divides the scattering into two parts of which one is due to air molecules only and varies as the inverse-fourth power of the wave-length and the other to particles in the air which scatter according to $\lambda^{-1.27}$. For our present purpose it does not make any great difference which of these two formulae we use except in the case of very hazy days.

With regard to changes in the emission from the sun, neither $\log(I_0 I_0')$ nor $\log(I_0'/I_0'')$ will remain absolutely constant, but it may be shown that variation in these values will lead to wrong values of $(\beta - \beta')$ and $(\beta' - \beta'')$, but will cause very little error in the amount of ozone deduced.

(b) *Measurements using the light from the zenith blue sky.* All the measurements of the height of the ozone layer indicate that the average height is about 45 to 50 km. At these heights the pressure will be about 10^{-3} of the surface pressure, and it is evident that, as MM. Cabannes and Dufay have pointed out, nearly all the light received from the zenith sky will have been scattered out of the direct solar beam by the atmosphere *below* the ozone layer except when the sun is very low. The absorption by the ozone will therefore be exactly the same as that in the direct solar beam, i.e. proportional to $\alpha \sec \zeta$. In this case there is obviously no fixed value corresponding to $\log(I_0 I_0')$ in the measurements on direct sunlight. It is found, however, that if $\log(I/I')$ for the light from the clear zenith sky be plotted against $\sec \zeta$ the points lie on a straight line (see figure 5, lines GH and $G'H'$) though the line is naturally different from that for direct sunlight. It is easy to calculate from this observed line, GH , and the amount of ozone (found from observations on direct sunlight) another line JK , figure 5, which will also be straight, representing the values of $\log(I/I')$ which would have been obtained from the measurements on the blue zenith sky if there had been no ozone present. This line will be the same for all clear days and may be used to determine the amount of ozone according to the formula

$$x = \{\log(I_z/I_z') - (\log I/I')\}/(\alpha - \alpha') \sec \zeta,$$

where $\log(I_z/I_z')$ is the value of $\log(I/I')$ given by the line referred to above for the

* Actually 3265 ÅU. is slightly absorbed by ozone and a correction is applied according to the approximately known amount of ozone present.

particular value of $\sec \zeta$ at the time of observation. On days when the sky is hazy the values of $\log(I/I')$ for the zenith sky may be corrected by means of the values of $\log(I'/I'')$ in the same way as for a cloudy sky (see below).

The light received from the clear zenith sky must be composed of light scattered from the direct solar beam by the atmosphere (1) below the ozone layer, (2) within the ozone layer, and (3) above the ozone layer. As indicated above, (1) may be expected to be predominant when the sun is high, but, as Dr Götz has recently pointed out, when the sun is low the light of short wave-lengths may be so reduced in passing through the ozone layer and by scattering that (2) and (3) become important. This seems to be the explanation of the fact that when observations on the clear

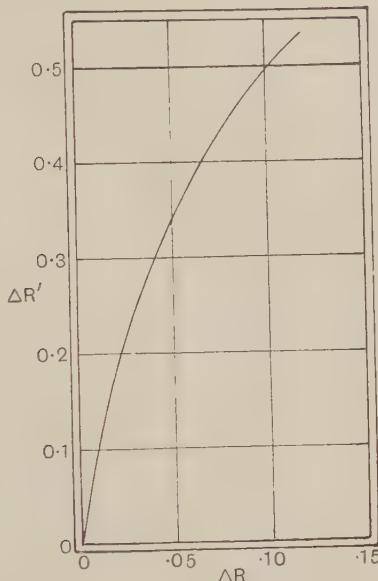


Fig. 6.

zenith sky are continued till the sun is nearly setting, it is found that while $\log(I/I')$ decreases at first, it afterwards becomes constant and finally increases again. Naturally the method of calculating the ozone breaks down when (1) ceases to be the only important part. An example of this is given by the last readings of October 5, shown in table 1.

(c) *Measurements of light from a thinly clouded sky.* The light illuminating the upper surface of a cloud layer will be partly direct sunlight and partly light from the sky, and these two have a very different spectral composition. The light received by an observer under the cloud layer, being a mixture of the lights from these two sources, will have a spectral composition intermediate between them, so that it is not possible to calculate the amount of ozone from measurements of $\log(I/I')$ alone. Since, however, clouds appear to scatter or absorb in the same proportion light of all of the three wave-lengths used by us, we may correct the observed values

Table I.

17. vii. 30	Time Sec ζ Ozone	10 : 05 1.295 0.279	10 : 22 1.264 0.276	10 : 30 1.247 0.277	10 : 35 1.239 0.278	10 : 40 1.230 0.277	11 : 39 1.174 0.283	11 : 53 1.170 0.285	11 : 59 1.168 (0.288)	16 : 48 2.04 0.281
3. x. 30	Time Sec ζ Ozone	09 : 45 2.105 0.191	11 : 10 1.795 0.193	11 : 14 1.785 0.194	11 : 24 1.770 0.196	11 : 32 1.770 0.195	11 : 45 1.765 0.196	11 : 50 1.760 0.195	11 : 59 1.755 0.197	
6. x. 30	Time Sec ζ Ozone	09 : 08 2.48 0.218	09 : 12 2.43 (0.221)	09 : 18 2.38 0.218	09 : 24 2.33 (0.222)	09 : 28 2.29 0.218	09 : 32 2.26 0.223	09 : 39 2.21 0.221	11 : 39 1.82 0.217†	11 : 44 1.82 0.221†
6. x. 30 (cont.)	Time Sec ζ Ozone	11 : 50 1.82 0.220†	11 : 51 1.82 0.217	11 : 54 1.82 (0.219)	12 : 32 1.84 0.218	13 : 02 1.90 (0.218)	15 : 45 2.64 0.220	—	—	—
7. x. 30	Time Sec ζ Ozone	11 : 49 1.83 0.198†	11 : 54 1.83 0.197*	12 : 00 1.83 0.198*	12 : 06 1.83 0.200	12 : 12 1.835 0.199†	12 : 30 1.865 0.200†	—	—	—
9. x. 30	Time Sec ζ Ozone	09 : 30 2.345 (0.244)	09 : 37 2.295 0.242	11 : 37 1.870 0.241	12 : 40 1.912 (0.242)	12 : 58 1.955 (0.239)	13 : 05 1.955 0.240	13 : 05 1.980 0.238	14 : 37 2.58 0.242	14 : 44 2.64 0.240
10. x. 30	Time Sec ζ Ozone	09 : 22 2.45 (0.221)	09 : 27 2.41 0.219	10 : 48 1.955 0.227†	10 : 52 1.945 0.218*	11 : 23 1.900 0.215*	11 : 46 1.88 0.216*	11 : 48 1.88 0.216*	11 : 52 1.88 0.208†	
10. x. 30 (cont.)	Time Sec ζ Ozone	11 : 56 1.88 0.217†	12 : 00 1.88 0.216§	12 : 03 1.88 0.222§	12 : 06 1.88 0.225§	12 : 10 1.88 0.220§	13 : 44 2.175 0.212	13 : 54 2.225 (0.215)	—	—
4. xi. 30	Time Sec ζ Ozone	09 : 12 3.61 0.257	09 : 54 3.01 0.256	09 : 58 2.965 (0.250)	11 : 09 2.55 0.249	11 : 20 2.50 0.249	12 : 34 2.565 0.242	12 : 38 2.59 (0.244)	13 : 20 2.81 0.241	
26. xi. 30	Time Sec ζ Ozone	11 : 20 3.23 0.223†	11 : 24 3.23 0.223†	11 : 34 3.19 0.220	11 : 38 3.19 (0.210)	12 : 00 3.18 0.221*	12 : 05 3.18 0.221*	12 : 09 3.19 0.221*	12 : 13 3.19 0.221*	12 : 16 3.21 0.220*
5. i. 31	Time Sec ζ Ozone	10 : 44 3.88 (0.222)	11 : 35 3.50 (0.219)	14 : 14 4.42 (0.221)	14 : 26 4.70 (0.218)	14 : 34 4.88 (0.217)	14 : 42 4.98 (0.216)	14 : 46 5.14 (0.214)	14 : 52 5.24 (0.213)	14 : 52 5.45 (0.211)
5. i. 31 (cont.)	Time Sec ζ Ozone	14 : 56 5.59 (0.209)	15 : 00 5.75 (0.206)	15 : 04 5.89 (0.206)¶	—	—	—	—	—	—

Plain figures denote observations on direct sunlight. Figures in brackets are observations on the zenith blue sky.

Figures in italics are observations on the cloudy zenith sky.

* = Observations through thin white cloud.

† = Observations through moderately thick grey cloud.

‡ = Observations through heavy grey cloud.

§ = Observations through rapidly changing cloud and were very variable, so that no good mean value could be obtained. The probability accounts for the large variation, based on the observations made during the time when the clouds were changing.

of $\log(I/I')$ by means of the observed values of $\log(I'/I'')$ in the following way and then calculate the amount of ozone as for observations made on blue sky.

From observations on clear days we can fix the lines *AB* and *JK* of figure 5. Let the difference between the values of $\log(I/I')$ for blue sky and cloudy sky at any one time be (ΔR) and let the corresponding values of $\log(I'/I'')$ be $(\Delta R')$. If observations are made on partially cloudy days a number of pairs of values of (ΔR) and $(\Delta R')$ may be obtained for approximately equal values of $\sec \zeta$ but with different types and thicknesses of cloud. If for each pair (ΔR) be plotted against $(\Delta R')$ the points are found to lie approximately on a curve such as that shown in figure 6. Then on a cloudy day, from a measurement of $\log(I'/I'')$ and the line *AB* of figure 5, we obtain $(\Delta R')$ and from a curve such as figure 6 we can read off (ΔR) and so correct the reading of $\log(I/I')$ to the value it would have had if the observations had been made on the clear blue sky. The ozone value is then calculated as for clear blue sky observations. As might be expected, such a curve of corrections does not hold exactly in all cases, but so long as the cloud is not very thick it appears that the errors introduced will seldom exceed 0.01 cm. of ozone.

A practical difficulty arises in using the light from a cloudy sky since it is necessary to make determinations of $\log(I/I')$ for exactly the same conditions as for $\log(I'/I'')$, and with certain types of cloud such as alto-cumulus or rapidly drifting fracto-cumulus the changes may be so rapid that this is almost impossible. In any case it is desirable to take at least three measurements each of $\log(I/I')$ and $\log(I'/I'')$ alternately and to use the mean values.

§ 4. DETAILED DESCRIPTION OF THE INSTRUMENT

In order that the instrument shall not be unduly heavy it is built of duralumin, but it still weighs about 50 kg. It is constructed as a double box with central diaphragm which makes it very rigid. The optical parts are mounted on one side of this double box and the amplifier occupies the other side. The whole instrument stands on three small legs so that it cannot be subject to any twisting forces which might distort it. The external dimensions of the instrument are 137 cm. long by 25 cm. wide by 30 cm. high. At present the focal length of the collimator lenses is 46 cm. and their diameter 5 cm. If other instruments are made it is intended to reduce the focal length while keeping the same diameter and to replace the mirrors by 15° reflecting prisms. This will reduce the length and weight of the instrument while increasing the light-gathering power.

The dispersion in the plane of the three central slits is about 23 ÅU. per mm. at 3200 ÅU. In fixing the slit-widths it is necessary to make a compromise, since if the slits are wide more light will be available, but if they are too wide the variation of a over the range of wave-lengths passed by S_2 will introduce appreciable errors unless a correction (depending on the value of $x \sec \zeta$) is applied*. The actual slit-

* The percentage error in ozone due to a finite slit-width, D , is proportional to $C^2 D^2 x \sec \zeta$, where C is the change of a with λ . For the slit-width adopted the error amounts to 1 per cent. when $x \sec \zeta = 1.36$, and is therefore negligible in most cases.

widths adopted were $S_1 = 0.22$ mm., $S_2 = 0.62$ mm., $S_3 = 1.20$ mm., $S_4 = 0.50$ mm., $S_5 = 2.5$ mm. Since the change of atmospheric absorption-coefficient with wavelength is much smaller for 3265 Å.U. than for 3110 Å.U., S_3 can be made wider than S_2 . The width of S_4 is immaterial since there is always ample light at that wavelength. S_5 need not be very narrow since it has merely to prevent stray light of other wave-lengths from falling on to the photoelectric cell.

Selection of wave-lengths. This again is a compromise. The shorter the wavelength set on S_2 the larger will be the value of α , but the smaller will be the amount of light available, and therefore the smaller the percentage accuracy with which it can be measured. It can be shown that, apart from variations of $(\beta - \beta')$, the greatest accuracy would be obtained if S_2 were set at about 3175 Å.U., but then the value of α would become rather small in relation to β and errors in the measurement of $(\beta - \beta')$ might lead to errors in the calculated quantity of ozone. Again, in order that $(\alpha - \alpha')$ may be large, S_3 should be set at a much longer wave-length than S_2 , but $(\beta - \beta')$ also is thereby made large while it should preferably be kept small. The exact setting of S_4 is of no great importance so long as it is within the region where the sodium cell is sensitive. The value of 3110 Å.U. for S_2 was chosen because there is a bright band in the solar spectrum here.

Optical details. The two halves of the double spectroscope must be in line so that the light travels straight through from one to the other, and the slits S_2 , S_3 and S_4 must be at right angles to this line; the focal plane of both spectroscopes will, however, be inclined to it. To get over this difficulty the wave-length 3110 Å.U. is focussed accurately on S_2 for both spectroscopes. The wave-lengths 3265 Å.U. and 4435 Å.U. would then come to a focus behind the slits S_3 and S_4 , so that additional lenses must be inserted in the paths of these rays to bring them to a focus on the slits. Figure 7 shows the detail of the central part of the instrument, the lettering being the same as in figure 1.

In order that all the light passing through S_2 and S_3 shall fall within the prism of the second spectroscope, a lens L_1 is placed immediately behind these slits and projects an image of the prism of the first spectroscope on to that of the second. As the slit S_4 is some distance from S_3 it is found best to add a small prismatic lens behind this slit for the same purpose.

A shutter (not shown in the figures), which can be operated from the outside, shuts off either S_2 or S_4 as desired. One of two neutral screens of different density can be inserted in the path of 4435 Å.U. when required by another lever also worked from outside. This is necessary since the value of $\log (I/I'')$ varies over a very wide range between the value for blue sky with high sun and the value for direct sunlight when the sun is low. The optical wedge is operated by means of a graduated dial on the top of the instrument and readings are taken from this dial.

The sector-wheel and commutator are driven by a gramophone motor since an electric motor would be liable to disturb the amplifier. The frequency of the alternations is about 30 ~. The brushes can be swung in order to get the best setting for the reversal of current.

Since the instrument cannot easily be carried by one person, and moreover has

to be taken out of doors, it is conveniently mounted on a trolley in which the necessary batteries also are carried. It thus forms a self-contained unit which can easily be moved about to any suitable position. With direct sunlight a quartz reflecting prism and lens are used to throw an image on to the slit. A ground quartz plate is generally inserted in front of the slit to even out the illumination and to reduce its intensity, since the energy is far too great for convenience except when the sun is low.

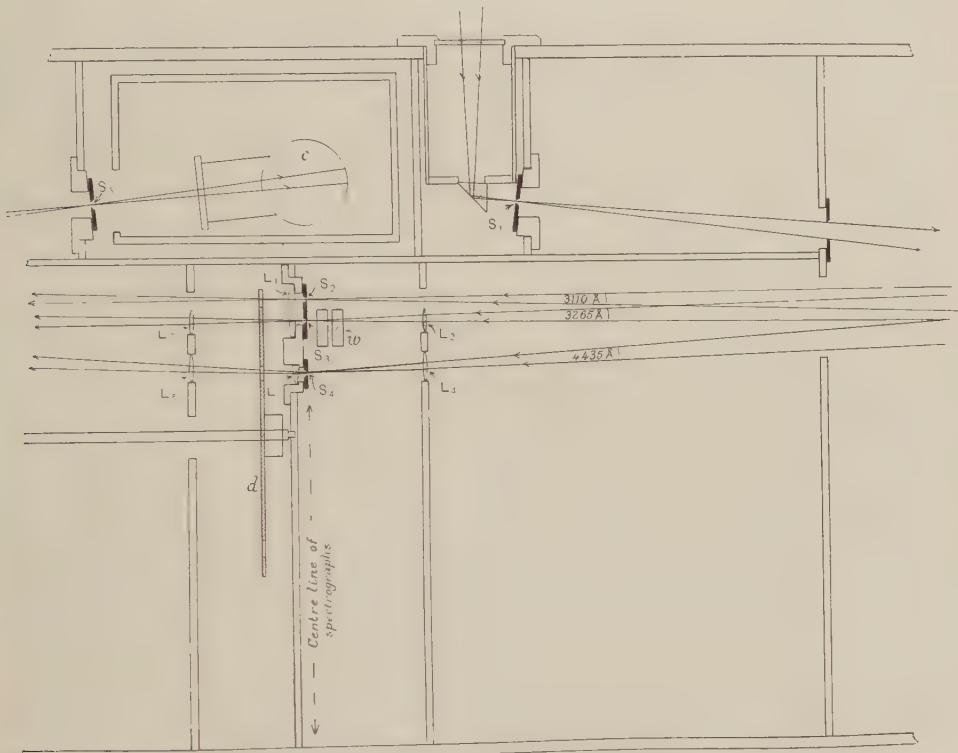


Fig. 7.

The present instrument is sufficiently sensitive to allow measurements to be made on the light from the clear zenith sky even when the sun is nearly on the horizon. One cannot calculate the ozone from such readings in the usual way, however, on account of the effect discussed at the end of § 3 (b). Observations on direct sunlight may be made until sec Z reaches about 7 or 8.

If an image of the full moon be thrown on to the slit with a quartz lens an appreciable deflection can be obtained on the galvanometer and very rough measurements of the amount of ozone can be made in this way when the moon is high.

§ 5. CALIBRATION OF THE INSTRUMENT

(1) *Wedge constant.* The constant of the optical wedge is given by the formula

$$K = d^{-1} \log (i_0/i),$$

i_0, i
 d

where i_0 and i are the intensities of light passing through two places on the wedge at a distance d cm. apart in the direction of the gradient of the wedge, when the wedge is uniformly illuminated. Fortunately it is exceedingly easy with the present instrument to determine this constant accurately. Both the slits S_2 and S_4 are blocked temporarily so that light only passes through S_3 . The galvanometer reading is then a measure of the intensity of light of 3265 ÅU. which reaches the photoelectric cell. A metal gauze which transmits a known percentage of the light falling on it is held over the window admitting light to the instrument and the galvanometer reading noted for a certain wedge setting. The metal gauze is then removed and the wedge adjusted till the same galvanometer reading is obtained. The shift of the wedge then corresponds to the transmission of the gauze. This test can best be made on a uniformly clear day, using the light from the zenith sky.

(2) *Determination of $\log (I_0' I_0')$ and $\log (I_0'' I_0'')$.* This value can only be found by measurement of $\log (I' I')$ for a series of values of $\sec \zeta$ and extrapolation to find $\log (I_0' I_0')$. As part of the atmospheric absorption is due to ozone high in the atmosphere and part to scattering low down, a plot of $\log (I' I')$ against either $\sec Z$ or $\sec \zeta$ will not give quite a straight line, but it can be shown that if $\log (I' I')$ be plotted against values of $\sec \zeta$ which correspond not to the true height of the ozone but to a slightly lower level (for the wave-lengths used here to 40 km. instead of 50 km.) then the points should fall very closely on a straight line, and when extrapolated this line will give the correct value of $\log (I_0' I_0')$. The value of $\log (I_0'' I_0'')$ is obtained in the same way but by the use of $\sec Z$.

§ 6. ACCURACY OF MEASUREMENT

The possible errors of measurement can be divided into two classes, (a) those due to instrumental imperfections, and (b) those due to atmospheric causes.

(a) *Instrumental.* The values of $\log (I_0' I_0')$ and $\log (I_0'' I_0'')$ found from a set of observations on one day depend on the constancy of the atmosphere during the observations, and the values found on different days will naturally differ somewhat for this reason. In so far as the changes are fortuitous, the mean value can be obtained with any required accuracy by means of observations taken on a sufficiently large number of days. If, on the other hand, there is a regular change throughout the day such as a diurnal variation of the amount of ozone, the values will be systematically wrong so that the error cannot be reduced by taking a large number of observations. Apart from such a systematic error, the value of $\log (I_0' I_0')$ should easily be obtained correct to within 0.005. As the variations of $\log (I' I')$ are much greater than those of $\log (I' I')$, the value of $\log (I_0'' I_0'')$ cannot be obtained with as great accuracy, but as an error in this quantity has little effect on the calculated ozone value, no appreciable error in the ozone content will be introduced. The error in the ozone value

due to an error in $\log(I_0/I_0')$ is inversely proportional to $\sec \zeta$. Under the most unfavourable conditions the error in ozone due to non-systematic error in $\log(I_0/I_0')$ will not exceed 0.005 cm.

Gelatine wedges, such as we use here, cannot be made with a density gradient which is strictly uniform at different parts of the wedge, but the error in the ozone from this cause is not likely to exceed 0.003 cm., and, if necessary, the wedge can be calibrated along its length.

The error in setting the wedge so that the current in the output circuit is zero, is governed by the unsteadiness of the galvanometer which cannot be entirely eliminated. It will naturally be inversely proportional to the intensity of the light available. When using direct sunlight, the percentage error in ozone due to this cause increases about 4.4 times for each increase of 1.0 in $\sec Z$. The error increases less rapidly with increasing $\sec Z$ when observations are made on the clear zenith sky. With an artificial light which could be kept constant and was roughly equivalent in intensity to that received from the clear sky when $\sec Z$ is about 8, it was found that the probable error of setting was under 0.005. Thus, for measurements when the sun is higher and more light is available, the error from this cause is quite negligible.

(b) *Atmospheric.* In observations on direct sunlight the effect of changes in the transparency of the atmosphere can be accurately allowed for and the chief errors should be those inherent in the instrument itself. In those on the light from the clear zenith sky the effect of haze will be similar to the effect of cloud and can be allowed for in the same way, but there is always some doubt whether a curve such as that in figure 6 will hold accurately under all conditions. In order to see what actual agreement would be obtained between observations taken at fairly close intervals of time, when the amount of ozone would probably not have changed much, the series of observations shown in table 1 were made. It will be seen that the agreement is very satisfactory, and that even when observations are made on a cloudy sky the error (the results from clear-sky observations being taken as correct) is nearly always under 0.01 cm. of ozone. For the purpose of studying the distribution of ozone in different meteorological conditions an error in reading of 1 per cent. is unimportant, so that it is seen that the new instrument allows observations of the amount of ozone to be made in all cases when the sun is more than about 12° above the horizon when the sky is lightly clouded, and when the sun is much lower with clear skies. If, therefore, it is found possible to arrange for a number of these instruments to be made and daily observations to be taken at a dozen or more stations distributed over N.W. Europe, the results which will be obtained in the course of a year or two should give us a thorough knowledge of the variation of ozone with pressure conditions. Whether or not this will lead to any knowledge of the formation and subsequent behaviour of cyclones and anticyclones it is naturally impossible to say at present, but in view of the closeness of the relationship which has already been found, and the value of any such knowledge if it could be obtained, it seems most highly desirable that the necessary instruments should be made and the observations carried out.

§ 7. ACKNOWLEDGMENTS

Even though the instrument was constructed in this laboratory, the cost of the materials and optical parts both for the final instrument and the preliminary investigations was very appreciable and I am greatly indebted to the Council of the Royal Society for a grant to cover these expenses.

DISCUSSION

Prof. A. O. RANKINE asked what was the frequency of commutation? Was it lower than that of the amplifier noises, so that the former could be amplified without the latter?

Mr J. GUILD. It is a great advantage to be able to obviate, in the manner described by the author, the tedious reduction of spectrum photographs involved in the older method. Would there be much difficulty in adapting the apparatus to the comparison at any desired pair of wave-lengths instead of only at a fixed pair as required for its present purpose?

Has it been experimentally verified that the relative sensitivity of the photoelectric cell for the two wave-lengths in question is independent of the actual intensity of the radiation? This would, of course, be the case with vacuum cells, in which, for each wave-length, the photoelectric current is proportional to the intensity, but it does not appear to be necessarily the case with gas-filled cells, such as are here used, if the current intensity curves for the two wave-lengths are appreciably curved within the range of intensities at which the measurements are made.

Sir A. S. EDDINGTON. I should like to ask how rapidly the amount of ozone in the atmosphere changes. If it changes in a few hours, that must create a difficulty in using observations of the sun at different altitudes for standardization purposes, especially if there is a systematic variation according to the time of the day. There is a current belief that the ozone tends to disappear in the night, and a few years ago it was suggested that in high latitudes during the long polar night it might disappear altogether —to the immense advantage of astrophysics—but I understand that the belief is quite erroneous.

AUTHOR's reply. Replying to Mr Guild, I do not see any reason why an instrument should not be made on the principle of the one now described, but with the slits capable of adjustment to different wave-lengths. There might be some small mechanical difficulties, but it is not beyond the powers of the British instrument-maker to overcome them. With regard to the second part of the question, I have not actually tested the relative sensitivity of the cell to different wave-lengths with different intensities of illumination, but it is very unlikely that there would be any change.

With regard to the President's question, it is found that the amount of ozone present may, at times, change by 10 per cent. or more during a day, and for this reason it is necessary to choose suitable days for the calibration of the instrument

and also to use the mean of the results from a number of sets of observations. It is not yet certain, but it is probable, that there is little difference in the amount of ozone present by day and by night; it is definitely known that there is not a markedly smaller amount at night. The amount of ozone during the polar night also is almost certainly above the average for the whole world.

In answer to Prof. Rankine, the frequency of the shutter admitting the two wave-lengths alternately is about 30 per second.

THE TUBE EFFECT IN SOUND-VELOCITY MEASUREMENTS

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ABSTRACT. The modifications of Kirchhoff's formula required to take account of the finite thermal conductivity of the tube, slip between the gas and the walls, temperature-discontinuity between the gas and the walls, and absorption of energy by the walls are calculated and are found to be negligible. The effect of roughness of the walls is discussed, and the conclusion is drawn that the large tube-effects often found in practice are due to irregular motion of the gas. It is argued that the methods of correcting for the tube-effect used hitherto are unreliable. The effects of oscillation of the piston and of the gas behind the piston are investigated and it is shown that these may become appreciable in some forms of apparatus. The yielding of a tube of elliptical cross-section is calculated and is shown to have a negligible effect.

§ 1. INTRODUCTION

THE marked disagreement between the specific heats of gases as found by the sound-velocity method and those predicted from spectroscopic data, and found by the author by a constant-flow method, led him to investigate theoretically a number of factors affecting the sound-velocity in a tube*. The correction for the effect of the tube is the most uncertain part of the sound-velocity method, and may amount to a considerable percentage of the result, especially when this is expressed as a specific heat; for a change of 1 per cent. in the velocity means a change of 7 per cent. in the specific heat at constant volume in the case of air, and much more in the case of a gas of high specific heat. Very little theoretical work has been done on the subject since the papers of Kirchhoff⁽¹⁾ in 1868 and of Thiesen⁽²⁾ in 1907. On the other hand, a great deal of experimental work has been done, and with very discordant results; the only point of agreement being the inadequacy of Kirchhoff's formula to represent the results quantitatively. It must

* As an example of this disagreement, which is in all cases particularly great at high temperatures, we may take the case of oxygen. Values of C_v for this gas, as found by Partington and Shilling, and as calculated from the vibration frequency of the molecule, are tabulated below.

Temperature	0° C.	500° C.	1000° C.
P. and S.	5.04	5.18	5.34 cals./mol.
Theoretical	5.00	6.00	6.52 , ,

For nitrogen and carbon monoxide the divergences are in the same direction. The author's values for oxygen and nitrogen are in agreement with the theoretical values but are not given here as they are to be published elsewhere shortly, and the determinations are not quite finished.

be remembered that the tube effect can be determined directly for the case of air at room temperature only, for only in this case can the velocity in the free gas be measured. By the use of helium, argon, and neon, which can now be obtained fairly cheaply, the effect could be determined with certainty over a wide temperature range, for there is no reason to suppose that the specific heats of these gases vary from the value $\frac{3}{2}R$ except by small calculable amounts due to deviations from the perfect gas laws. The effect of varying viscosity and thermal conductivity might thus be investigated. Up to the present, however, this has not been done. The less certain methods which are the only ones available for other gases are discussed later.

§ 2. THE VELOCITY IN THE FREE GAS

There seems to be no reason to doubt that, if the frequency and intensity of the sound be not too high, the velocity in the free gas is given by $\sqrt{(\gamma p/\rho)}$ with small corrections for imperfection of the gas, where p and ρ are the pressure and density respectively. With high-frequency sound, however, the effects of viscosity and thermal conduction become appreciable even in the free gas, and there is the additional possibility that the rate of transfer of the internal energy between molecules may be too slow for the equipartition of energy to be maintained⁽³⁾. Thus Pierce⁽⁴⁾ found experimentally that the velocity in air had a high value at about 40,000 vibrations per second, and that in carbon dioxide it started to rise at a frequency of about 10^5 . It does not seem impossible that in gases whose molecules are more complicated the energy-exchanges might be slow enough to produce effects at lower frequencies.

 p, ρ

§ 3. THE VELOCITY IN AN INFINITELY LONG CYLINDRICAL TUBE

Experiment shows that the velocity of sound in gas contained in a tube is less than that in the free gas. It was early suggested that this was due to the finite viscosity and thermal conductivity of the gas, which will have much more effect in the neighbourhood of the walls of the tube than in the free gas. Helmholtz calculated the effect of viscosity and Kirchhoff⁽¹⁾ the effects of viscosity and heat conduction. The latter obtained the following expression:

$$\text{Velocity in tube} = a \{1 - \beta/2R\sqrt{(\pi n)}\} \quad \dots\dots(1),$$

where

$$\beta = \sqrt{\mu + (a/b - b/a)\sqrt{\nu}} \quad \dots\dots(2)$$

$$= \sqrt{(\eta/\rho)} \{1 + \frac{1}{2} \cdot \sqrt{(9\gamma - 5)} \cdot (\gamma - 1)/\sqrt{\gamma}\} \quad \dots\dots(3),$$

if we put $k/\eta c_v = \frac{1}{4}(9\gamma - 5)$. a, b
are the adiabatic and isothermal velocities, R
is the tube radius, n
is the frequency, η
is the viscosity, ρ
is the density, k
is the thermal conductivity, $\mu = \eta/\rho$ and $\nu = k/\rho c_v$. a, b R n η ρ k μ, ν

The assumptions which he made were: (a) That the gas in contact with the walls is at rest. (b) That the gas in contact with the walls is at the same temperature as the walls. (c) That the temperature of the walls is constant. (d) That there are no irregularities in the walls of the tube of sufficient size to produce appreciable irregular motion in the gas.

Kirchhoff expressed assumption (d) by saying that the walls were assumed to be "perfectly smooth." This expression seems to have given rise to some misunderstanding amongst subsequent writers, for we come across such statements as "The friction and heat exchange with the walls of the tube are not accounted for in Kirchhoff's formula"⁽⁵⁾. Assumptions (a) and (b) are equivalent to an assumption that the walls are what is called in text-books of mechanics "perfectly rough," i.e. that the coefficient of friction with the walls is infinite and that the heat transfer between the walls and the gas in immediate contact with them is perfect. Kirchhoff himself states that "If the smooth surface of the tube is made rough, the effect of viscosity as well as that of heat conduction must increase." Since he has already assumed that they are producing the maximum effect under the conditions postulated, this statement can only be true if the roughness is sufficient to upset assumption (d)—i.e. to produce irregular motion.

Before carrying the theoretical discussion any further let us see how far the results of experiments agree with Kirchhoff's formula. There is an extraordinary diversity of evidence amongst the work of the numerous experimenters, but the general results may be summarized as follows: (1) The formula is qualitatively correct in that the effect of the tube increases as the radius or the frequency decrease. (2) Though one or two experimenters have considered the formula to be quantitatively correct, the majority state that the actual effect of the tube is considerably greater than that given by Kirchhoff's formula. (3) The effect on the velocity depends largely upon the nature of the inner surface of the tube, being specially great if this is rough so that assumption (d) is upset. (4) The effect is not always inversely proportional to the radius. Partington has, however, pointed out that it may be difficult to insure that the tubes of different radii used have exactly the same type of surface. (5) The effect is not always inversely proportional to the square root of the frequency with a given tube. Thus Seebeck found that it varied as $n^{\frac{3}{2}}$. The evidence is summarized by Partington and Shilling, with many references, in *Specific Heats of Gases*, p. 53.

It is evident then that one or more of the assumptions (a), (b), (c) and (d) are not correct. As a matter of fact, in practice, none of them are correct. Let us consider them one by one.

(a) The assumption that the gas in contact with the walls is at rest involves the suppositions that the walls are at rest, and that there is no relative motion between the walls and the layer of gas immediately in contact with them: unless, of course, we suppose that the two motions cancel out, which is unlikely.

The effect of the yielding of the tube has been calculated by Lamb. The frequency of the simplest mode of radial vibration of a circular tube is given by $\sqrt{(H \rho_t)/2\pi R}$, where R , H , and ρ_t are the radius, Young's modulus, and density.

This works out at about 50,000 per second for a glass tube of radius 2 cm. Thus the frequency of the sounds used in practice are much lower than the resonance frequency for this vibration, the increase in diameter of the tube is almost exactly in phase with the pressure, and the inertia of the tube can be neglected. The effect on the velocity of the sound is consequently equivalent to a change in the elasticity of the gas, and is given by

$$\frac{\text{Velocity in actual tube}}{\text{Velocity in rigid tube}} = 1 - \frac{\gamma p R}{H \tau} \quad \dots\dots(4),$$

where τ is the wall thickness. For a glass tube of radius 2 cm. and wall thickness 2 mm., containing air at atmospheric pressure, the correction amounts to about 3 parts in 100,000 and so is negligible.

⁷

It is known that when a gas flows through a tube it behaves as if there was a slight slip between the gas next the wall of the tube and the wall, this effect being especially prominent at low pressures. Maxwell⁽⁶⁾ gave a formula for the extent of this slip in terms of the fraction of the molecules striking the boundary which are "specularly reflected," and showed that there will be slight slip even if this fraction is zero. The phenomenon has been experimentally investigated by Kundt⁽⁷⁾ and by Knudsen⁽⁸⁾. The effect of slip on the velocity of sound in a tube is worked out in the appendix, where it is shown that the only alteration in Kirchhoff's formula is a change in the viscosity term of β , equation (2), so that we now have

$$\beta_1 = \frac{\sqrt{\mu}}{1 + \pi \{(2-f)/f\} \sqrt{(2m\eta/p)}} + \left(\frac{a}{b} - \frac{b}{a}\right) \sqrt{\nu} \quad \dots\dots(5),$$

where f is the fraction of the molecules which are diffusely reflected. Thus the effect of slip is to diminish the effect of the tube on the velocity, i.e. to increase the velocity. Since f is not far from unity, we find that for air at one atmosphere and a frequency of 1000 ~, β is only altered by about 2 parts in 1000; which means about 2 parts in 100,000 of the velocity, if the tube correction is 1 per cent.

^f

Finally it remains to enquire whether there could be any apparent motion, relative to the wall, of the gas next the wall, in a direction normal to the surface. Lately many experiments have been done showing that when plane waves of sound are reflected from a solid surface there is a loss of energy in the reflected beam, particularly if the solid be porous. This may be due to scattering, to motion of the solid surface, or to viscous absorption of energy by the air in the pores of the solid; but whatever the mechanism, the effect, so far as the body of the air is concerned, is that of a motion of the layer of air next the surface such that the displacement towards the solid is a quarter of a period out of phase with the pressure at the surface, i.e. such that there is a velocity towards the wall proportional to the excess pressure at any instant. In the appendix, an expression is derived giving the effect of such motion at the walls on the velocity of sound. It is shown that we must add two extra terms to Kirchhoff's equation, (1), thus:

$$\text{Velocity of sound} = a \left\{ 1 - \frac{\beta}{2R \sqrt{(\pi n)}} + \frac{\nu \chi'}{a^2 R} - \frac{1}{8} \left(\frac{\gamma \chi'}{\pi n R} \right)^2 \right\} \quad \dots\dots(6),$$

^{x'}

where the radial velocity at the walls = $\chi'(p - p_0)p_0$. The ratio of the radial amplitude at the walls to the longitudinal amplitude at the centre of the tube is easily shown to be $\chi'\gamma'a$. From this we find that if the term in $v\chi'$ is to produce a change of 1 part in 1000 in the velocity, the ratio must be about 500 : 1 which is obviously impossible. For the term in χ'^2 to produce such an error, with a tube of radius 2 cm. and a frequency of 3000 ~ (as in Partington's experiments), the ratio need be only 1 : 20, which might be possible with a porous tube. It is shown in the appendix, however, that the amplitude of a progressive wave decreases, as it passes along the tube, proportionally to $\exp(-\gamma\chi'v aR)$, which would mean in this case that the amplitude would diminish to one-twelfth for every metre of its path. Thus, even with only half a metre between the source of sound and the reflecting stop, the reflected waves would only have one-twelfth of the amplitude of the direct waves near the source; and resonance would be practically undetectable. So that if it is possible to use a given tube we may be sure that the error due to absorption of energy by the tube is less than 1 in 1000.

(b) It is known that when heat is being transferred from a gas to a solid surface there often appears to be small but finite temperature-jump at the boundary. This phenomenon is especially evident at low pressures and corresponds to the phenomenon of slip mentioned above, though it is considerably more difficult to deal with theoretically. It obviously invalidates Kirchhoff's assumption (b). In the appendix the effect of this on Kirchhoff's formula is shown to be merely an alteration in the conductivity term in β , so that

$$\beta = \sqrt{\mu} + (a/b - b/a)\sqrt{v}/\{1 + 3\sqrt{(\pi n k \rho c_p)}\zeta\} \quad \dots\dots(7),$$

where ζ is the rate of heat-transfer across unit area of the boundary if the temperature-jump is one degree. It follows from this that the greater the temperature-jump (i.e. the smaller ζ) the less is the effect of the tube on the velocity, and the greater is the velocity. This we should have anticipated; since the temperature-jump at the boundary means that the compressions and expansions will be more nearly adiabatic than would otherwise be the case.

If we substitute in this expression Knudsen's formula* for the temperature-jump, we get $\zeta = (k/1.9\lambda) \cdot 2g/(2-g)$ where g is an accommodation coefficient analogous to the f in equation (5), and λ is the mean free path of the molecules of the gas. Hence

$$\beta = \sqrt{\mu} + (a/b - b/a)\sqrt{v}/\{1 + 2.8\lambda(2-g)/g \cdot \sqrt{(\pi n \rho c_p/k)}\} \quad \dots\dots(7a).$$

For air at room temperature, and a frequency of 3000 ~, we find that the conductivity term in β is decreased by about 1 per cent., so that the effect on the sound-velocity is negligible.

(c) Kirchhoff's assumption that the walls of the tube are at a constant temperature is equivalent to assuming that they have an infinite thermal conductivity or an infinite specific heat. Actually, rapidly damped temperature-waves will pass from the inner surface of the tube for a short distance into the thickness of the wall, so that the temperature of the inner surface does not remain constant. In

* See e.g. Knudsen, *Ann. der Phys.* **34**, 593 (1911) or Hercus and Laby, *Phil. Mag.* **3**, 1061 (1927).

in the appendix it is shown that the effect of this is to decrease the conductivity term in β thus:

$$\beta = \sqrt{\mu} + (a/b - b/a) \sqrt{v / \{1 + \sqrt{(k\rho C_p / \kappa \rho_r C)}\}} \quad \dots \dots (8),$$

where k , ρ , and C_p are the thermal conductivity, density, and specific heat at constant pressure per gm. of the gas, and κ , ρ_r , and C are the corresponding quantities for the tube.

For glass and air under atmospheric pressure the correction to β is of the order 1 : 600, so that the effect on the velocity will be of the order 1 : 60,000 (I assume a tube correction of 1 per cent.) and is negligible.

We thus see that the invalidity of Kirchhoff's three assumptions (a), (b) and (c) (see p. 342) cannot appreciably affect the accuracy of his formula, and cannot account for the experimental results. In fact the effects of slip, bad heat-transfer between gas and tube, and finite conductivity of the tube not only are negligible but go in the wrong direction, for nearly all experimenters agree that the effect of the tube is greater than that predicted by Kirchhoff's formula. We are thus driven to suppose that the cause of the variations lies in the irregular motion of the gas or in some cause unknown. Partington and Shilling claim⁽⁹⁾ that Stürm's experiments⁽¹⁰⁾ and their own show that the velocity is dependent on the material of the tube; but this argument suffers from the same objection that Partington and Shilling have themselves pointed out when discussing experiments on the effect of variation of the tube radius: the conductivity was not the only variable in these experiments, for this could not be altered without the surface being altered as well. That irregular motion of a sort not accounted for in Kirchhoff's theory does occur in resonance tubes appears to be shown by the recent experiments of Andrade⁽¹¹⁾ and Pringle⁽¹²⁾, who watched individual dust particles in a Kundt tube. From the sinusoidal tracks of particles shown in the photograph which accompanies Andrade's letter to *Nature*⁽¹¹⁾, it is evident that some of the particles had steady radial velocities equal to about one-sixth of their maximum vibrational velocity: though whether this indicated a motion of the gas, or a motion of the particle relative to the gas, I do not know. This must result in extra dissipation of energy and might well also affect the sound velocity. It is well known that when a stream of gas is flowing through a tube there is a certain velocity above which the steady streamline motion becomes unstable, and eddy motion sets in at the slightest disturbance. It does not seem unreasonable to suppose that the same might hold for the oscillatory motion in a resonance tube*; though owing to the very different velocity-distribution across the tube in the two cases, the critical velocity would probably be quite different. Slight irregularities in the tube might well cause such eddy motion to set in; and, indeed, the observed dependence of the velocity on the surface shows that the effect is aggravated, if not caused, by irregularities in the surface. It is possible that the effect might be avoided by the use of much smaller sound-intensities, and, if necessary, of an amplifier to detect resonance. The maximum air velocity might thus be reduced below the critical value. We can form an estimate of the size of the irregularity required by noting that at a distance

k, ρ, C_p
 κ, ρ_r, C

* Since this paper was read Prof. Andrade has published a second letter to *Nature*, 127 (1931) in which he shows photographs of such vortices in a sounding tube.

of $2\pi \sqrt{(2\mu/n)}$ from the wall the amplitude of the oscillations is only about 0.002 of its value at the centre of the tube⁽¹³⁾. For air, and a frequency of 3000 ~, this distance is about 0.25 mm., and it does not seem that irregularities of a grain-size less than this could produce much effect, since they would be situated in comparatively still air*. This does not necessarily mean that the irregularities must project more than this distance into the tube in order to produce an effect, for if they were of considerable area their effect could penetrate beyond it. The point is that mere roughness should not produce such a large effect as a slightly wavy surface. In this connexion it is worthy of note that Cornish and Eastman⁽¹⁴⁾, two of the very few observers who have confirmed Kirchhoff's formula, used metal tubes which, though rougher than glass tubes, would be less prone to waviness.

Let us now consider the bearing of the above discussion on the determination of specific heats. The use of a tube to contain the gas can hardly be avoided except for air at room-temperature unless we use very high frequencies, which would introduce other errors. Hence a tube correction is necessary; and we can get an idea of its importance from the facts that in the experiments of Partington and Shilling⁽¹⁵⁾ on air, oxygen and nitrogen, it varied from about 0.07 to 3.6 per cent. of the velocity, i.e. from 0.5 to 25 per cent. of C_v .

Three methods, other than the use of Kirchhoff's formula, have been tried for determining the correction. Of these the first is to use tubes of two or more different diameters and to extrapolate to the case of infinite diameter, either by assuming that the tube correction varies inversely as the diameter as in Kirchhoff's formula, or empirically, using several tubes. The uncertainty of the true dependence of the correction on the diameter and the fact that the perfection of the surface will vary from tube to tube make this method quite unreliable.

The second method is to use only one tube but several frequencies, and to extrapolate to infinite frequency, either by assuming that the correction varies inversely as the square root of the frequency, or empirically. Here again the trouble is that the correction does not always obey the above rule; and extrapolation under such circumstances is uncertain.

The third method is to abandon that part of Kirchhoff's formula which deals with R and n , but still assume that the correction is proportional to β . The correction is determined experimentally for air at room-temperature by making use of the determinations of the velocity in free air. For air at other temperatures and for other gases the above assumption is made. So far as the author is aware, no justification has been brought forward for this assumption. Seeing that the correction for air at room-temperature for one of Partington and Shilling's tubes was 14 times, and for another tube was only 1.05 times that given by Kirchhoff's formula, the retention of even a part of this formula requires justification; especially when, in one case, the correction amounted to about 25 per cent. on the specific heat! If we assume that the true correction for a given gas is known at 0° C., and if the value of γ for the gas does not vary much with temperature, then the procedure is equivalent to assuming that the correction is proportional to $\eta \rho$ for all temperatures. Now

* See, however, the remarks of Dr Richardson and the author's reply in the discussion at the end of this paper.

several experimenters have stated that the effect of the tube is not inversely proportional to \sqrt{n} ; for instance Seebeck⁽¹⁶⁾ found it varied as $n^{-\frac{3}{2}}$. If this be so, and if, as has been shown above, the only properties of the tube which can affect the velocity are its size and shape (I include roughness in this); both being properties requiring lengths only to define them, the theory of dimensions shows that the correction cannot be proportional to η/ρ , as this would require the time dimensions to be wrong. Even if, with a given value of γ , the correction were proportional to η/ρ it is difficult to see why the effect of the tube should be divided between the viscosity effect and the conductivity effect in the same ratio as that given in Kirchhoff's formula, in spite of the fact that the correction is sometimes 14 times too large. In other words, even if the dependence on η/ρ were correct, it is improbable that the dependence on γ would be so.

Before leaving the subject of the tube correction, we may point out that where, as in Dixon's experiments, the group-velocity is measured in place of the wave-velocity, the magnitude of the correction will depend upon the way in which the velocity varies with the frequency. The group-velocity is given by

$$U = V - \lambda dV/d\lambda \quad \dots\dots(9), \quad U$$

$$\text{or} \quad U = V + ndV/dn \text{ if the difference is small} \quad \dots\dots(10).$$

V is here the wave-velocity. Application of this formula gives at once the result that if the effect of the tube varies inversely as \sqrt{n} , then the correction to be added to the observed group-velocity is one-half of that which would be required for the wave-velocity at about the same frequencies. If the tube effect varied as $n^{-\frac{3}{2}}$ the correction would also be half that required for the wave-velocity, but would have to be subtracted instead of added. The fact that Dixon found that the velocity was less in the tube than in free air apparently shows that, in his case at least, the tube effect could not have varied according to a higher inverse power of n than n^{-1} . The above formula for the group-velocity applies, however, only to a sound whose components lie within a narrow frequency range. A pulse would change its form as it progressed, and no very definite conclusion can be drawn.

It appears, then, that much systematic experimental work will have to be done before great faith can be placed in the results of sound-velocity determinations in tubes.

§ 4. THE VELOCITY IN A TUBE OF FINITE LENGTH

Having discussed the factors which must be taken into account in any method of measuring sound-velocity in a tube, we will now consider a few of the—less important—effects due to the ends of the tube. It is fairly obvious that the ends will not appreciably affect the velocity of a progressive wave in the tube except in their immediate neighbourhood. They will not, therefore, alter the distances between adjacent nodes in the middle of the tube, though they will determine the positions of these nodes. It follows that the dust-figure methods are unaffected by end-errors, though end-corrections are necessary with certain resonance methods.

Thiesen⁽¹⁷⁾ has shown that in the use of his method, in which the whole length of the resonator and the frequency are measured, an extra term depending on the

l length of the resonator must be introduced into Kirchhoff's expression. Thus if *l* be the length of the resonator,

$$\text{Velocity} = a\{1 - \sqrt{\mu/2R}\sqrt{(\pi n)} - (1/R + 2/l)(a/b + b/a)\sqrt{\nu/2}\sqrt{(\pi n)}\} \dots (11).$$

It will be seen that the extra correction becomes negligible for the long tubes used by most experimenters; and in any case the equation is of little more use than Kirchhoff's equation, to which it reduces when *l* = ∞.

D''

Of more interest is it to enquire whether vibration of the end of the tube can affect the results. It is shown in the appendix that only that component of the motion of the stop which is in phase with the gas pressure (i.e. the component which absorbs no energy from the gas) can affect the positions of the nodes. If *D''* be the velocity-amplitude, per unit pressure-amplitude in the gas, of this component of the stop's motion, then the position of the nodes and antinodes are given by

$$\tan 4\pi x/\lambda = 2\sqrt{(\rho E)} D'' \dots (12),$$

x, E

where *x* is the distance from the stop, while *E* = *yp* and is the elasticity of the gas. Thus, providing that *D''* remains constant, the distances between the nodes are equal to the half-wave-length in the gas, and no error is introduced. In some experiments, however (e.g. those of Partington and Shilling), the stop is moved along to obtain the various resonance points, so that the free length of the rod or tube which supports it varies during the experiment. It is shown in the appendix that if we neglect the mass of the piston itself, *D''* is given by

$$D'' = \frac{1}{2\pi n\rho'} \cdot \frac{\mu^{-1} \sinh(2l/\mu) - 2\pi\lambda'^{-1} \sin(4\pi l/\lambda')}{\cosh(2l/\mu) + \cos(4\pi l/\lambda')} \cdot \frac{A_p}{A_r} \dots (13),$$

p', l, λ'
*μ**A_p, A_r*

where *p'* is the density of the piston-rod, *l* is its free length; *λ'* is the wave-length of the sound in the rod, *μ* is the distance which waves must travel along the rod before they are reduced to *e*⁻¹ times their original amplitude (i.e. an inverse measure of the damping), and *A_p*, *A_r* are the areas of cross-section of the piston and rod respectively.

If *λ'/μ* be small, as it probably is in practice, this can be simplified and we get

$$\tan\left(\frac{4\pi x}{\lambda}\right) = \sqrt{\left(\frac{\rho E}{\rho' H}\right) \cdot \frac{A_p}{A_r} \cdot \frac{(λ'l/\pi μ^2) - \sin(4\pi l/\lambda')}{l^2/\mu^2 + \cos^2(2\pi l/\lambda')}} \dots (14),$$

H

where *H* is Young's modulus for the piston-rod. The fraction on the right is shown plotted against *l/λ'* in figure 1 for the case in which *λ'/μ* = $\frac{1}{2}$.

It is difficult to form an estimate of the value of *λ'/μ* in practice; but whilst the extreme peaks of the curve are greatly dependent on *μ*, being higher as *μ* is greater, the remainder of the curve is almost independent of *μ*. Since the errors are small, $\tan(4\pi x/\lambda)$ is nearly equal to $4\pi x/\lambda$ for the first node, and we can regard the graph as giving directly the displacement of the nodes for various positions of the piston. For air and a silica rod, if *A_p/A_r* = 30 the ordinates of the above curve must be multiplied by about 3×10^{-5} to give the ratio of the displacement to the wave-length. Also if the frequency is 3000, *λ'* is about 170 cm., so that the above graph corresponds to the range *l* = 0 cm. to *l* = 170 cm. The conditions mentioned

are roughly those holding in Partington and Shilling's experiments with silica tubes. It is evident, then, that except near the resonance points for the piston-rod, the errors in setting are of the order of 0.01 mm. and can be neglected. If a reading were taken near a resonance point, however, an appreciable error might result.

Another vibratory system sometimes coupled to that of the gas in the resonance tube is the gas which is contained in the tube behind the piston. If the latter is made smaller than the bore of the tube, as it often is to avoid its rubbing against the tube, there will be an interchange of energy between the systems. In the appendix it is shown that the proportional error introduced by this effect is approximately equal to

$$-\alpha / \{ 1 - \mathcal{R} + B \sin 2\theta + (\mathcal{R} - 1/\mathcal{R} - B^2/\mathcal{R}) \sin^2 \theta \} \quad \dots \dots (15),$$

where α is the fractional difference between the sound-velocities on the two sides

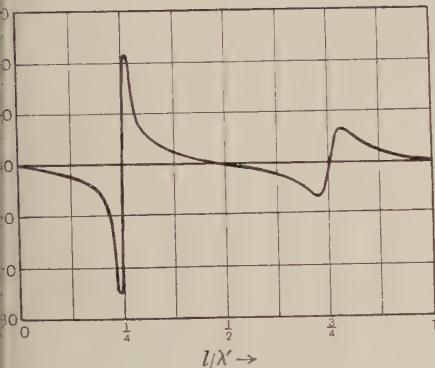
 α 

Fig. 1.

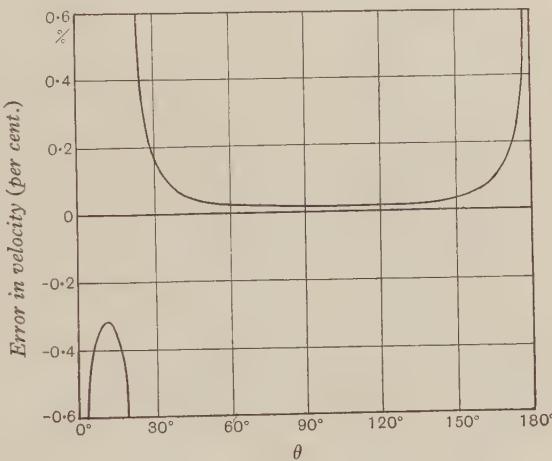


Fig. 2.

of the piston, due to the presence of the piston-rod, \mathcal{R} is the ratio of the cross-sectional areas of the gas-spaces in front of the piston and behind it, $B = 2\pi^2 R^2 / \lambda C$, C is the acoustic conductivity of the annular space between the piston and the walls of the tube, and θ can be taken as equal to $(2\pi L/\lambda - N\pi)$, where L is the total length of the tube.

If \mathcal{R} is nearly unity (that is, if the piston-rod is much smaller than the tube) and B^2/\mathcal{R} is much greater than unity, we can write the above expression

$$\alpha/B (B \sin^2 \theta - \sin 2\theta) \quad \dots \dots (16).$$

To get a rough estimate of the value of α we will assume that the effect of the tube and piston-rod on the sound-velocity is proportional directly to the combined perimeters of their cross-sections and inversely to the area of the cross-section of the gas-space between them. This would follow from the simple theory of the effect given in Rayleigh's book on sound⁽¹⁸⁾. If R and r are the radii of the inner surface of the tube and of the piston-rod respectively, and if the effect of the tube alone

 \mathcal{R}
 B, C θ, L R, r

v_0, δ

is given by $v = v_0(1 - \delta)$, the effect of the tube and piston-rod together should be given by

$$v' = v_0\{1 - R/(R - r).\delta\}, \quad \dots\dots(17).$$

 v'

where v' is the sound-velocity in the space between the tube and piston-rod.

Thus

$$\alpha = r\delta/(R - r) \quad \dots\dots(18).$$

We also have

$$\mathcal{R} = R^2/(R^2 - r^2) \quad \dots\dots(19).$$

In Partington and Shilling's silica apparatus $R = 2$ cm., $r = 0.5$ cm. and $\delta = 0.009$, so that $\alpha = 0.003$ for air at room temperature, and $\mathcal{R} = 16/15$.

It is difficult to calculate a value for the acoustic conductance of the space between the piston and the wall, so it was determined experimentally by construction of an accurate model of the piston and tube walls. This was filled with a solution of an electrolyte, two large electrodes were inserted some distance away on either side of the piston, and the electrical resistance between them was measured with and without the piston. The specific resistance of the solution was measured also; and this, divided by the increase in cell-resistance due to the piston, gave a quantity numerically equal to the acoustic conductivity of the gap. The result came out as 1.5 cm. For a wave-length of 10 cm., used by Partington and Shilling in the case of air at room temperature, this makes B equal to 5 nearly. Thus we can use expression (16) in place of (15). In figure 2 the percentage error in the velocity has been plotted against θ for these values of α and B .

An increase of π in θ corresponds to change of tube-length or of wave-length of about $2\frac{1}{2}$ per cent. for a 2-metre tube and a wave-length of 10 cm. It will be seen that the error is about 0.015 per cent. over about half of the range but that it is greater than 0.3 per cent. over about a sixth of the range. It would be difficult to predict in advance on what part of the range θ would lie for any given wave-length and tube. It is not claimed that the above theory gives anything but the order of magnitude of the effect; but it does at least show that the effect has to be reckoned with. It could be diminished by allowance of as small a gap as possible between the piston and the walls, or by the use of a piston of considerable thickness.

§ 5. THE VELOCITY IN A TUBE OF IMPERFECT SHAPE

We have already mentioned the possible effect of small irregularities in the tube wall. When there are variations in the bore of the tube extending over lengths greater than the radius of the tube it is possible to make an approximate calculation of their effect if no irregular motion of the gas is produced. Lord Rayleigh has shown in his book on sound⁽¹⁹⁾ that in the case of a tube which departs slightly from the cylindrical shape, the deviations of the nodes from their normal positions are given by

$$\Delta l = \int_0^l \cos \frac{2\pi mx}{l} \frac{\Delta s}{S_0} dx \quad \dots\dots(20),$$

$l, m, S_0, \Delta s$

where l is the length from one end of the resounding tube to the m th node; S_0 is the mean cross-sectional area; and Δs is the difference between the actual area at any position and the mean.

To take an example, let us suppose that for a distance of $\lambda/4$ on one side of a given node the diameter of the tube is 1 per cent. greater than the mean. Then that node will be displaced by a distance

$$\int_{\lambda/4}^{\lambda/2} \cos \frac{4\pi x}{\lambda} \cdot \frac{1}{50} dx, \text{ which} = \frac{\lambda}{100\pi} \quad \dots\dots(21).$$

Deviations greater than 1 per cent. in the diameter may be expected in glass and silica tubes. Errors due to this, however, will tend to cancel out if many nodes are measured and the mean distance between them obtained in the best way. This will not be the case, however, if the mean is obtained by taking the distances of all the nodes from the first node, dividing each by the appropriate number of half-wavelengths, and taking the mean, for in this case an error in the position of the first node would be reproduced *in toto* in the mean.

The last effect to be discussed is that of the yielding of a tube whose cross-section is not circular. As has been stated above, Lamb showed that the yielding of circular tubes produced a negligible effect; it is not immediately evident, however, that the same would apply to an elliptical tube, since bending as well as stretching would take place. In experiments where the tube is coiled round in a spiral, as in those of Dixon, the cross-section is almost certain to be slightly elliptical. Dixon showed experimentally that there was no measurable difference between the sound-velocities in a leaden tube when straight and when coiled. It was thought worth while to show mathematically that this will be so with all tubes. It is shown in the appendix that the fractional effect on the velocity is given by

$$-\frac{\gamma P}{H} \left(\frac{b}{t}\right)^3 \epsilon \quad \dots\dots(22),$$

where H is the Young's modulus for the tube material, b is the semi-axis major of the ellipse, t is the wall thickness and

$\epsilon = 2f^{-1} \{12\pi^{-1}\beta^2Ef^4 - 3/8 \cdot \beta f^2(1-f^2)(5+3f^2) + 3/64 \cdot (1-f^2)^2(7+5f^2)\} \dots(23)$,
where f is the ratio of the minor to the major axis of the ellipse; β is a certain function of f whose value is given in Timoshenko's *Elasticity*⁽²⁰⁾ and E is an elliptic integral of the second kind giving the ratio of half the perimeter of the ellipse to the major axis and depending upon f . Values of these are tabulated below for a few values of f .

Table

f	β	E	ϵ
1.0	0	$\pi/2$	0
0.9	0.57	1.492	0.014
0.8	0.133	1.417	0.054
0.6	0.391	1.278	0.204

If we put $\gamma = 1.4$, $P = 10^6$ dynes/cm.², $H = 6 \times 10^{11}$ dynes/cm.², we get

$$\begin{aligned} \text{Fractional effect on velocity} &= -3.2 \times 10^{-8} \cdot (b/t)^3 \text{ if } f = 0.9 \\ &= -12.4 \times 10^{-8} \cdot (b/t)^3 \text{ if } f = 0.8 \\ &= -4.6 \times 10^{-7} \cdot (b/t)^3 \text{ if } f = 0.6. \end{aligned}$$

H, b
 t
 ϵ
 f, β
 E

It will be seen that even if we suppose f to be 0.6 and b/t to be 10, the effect is only about 1 part in 2000; and these conditions are extreme. In practice, then, we can at ordinary pressures neglect the effect of the yielding of the tube whether it be of circular or elliptical cross-section.

MATHEMATICAL APPENDIX

(i) *Kirchhoff's wave equations.* For the case of waves symmetrical about an axis, and assuming that the three quantities u , s , and $\theta \propto e^{i\omega t}$, Kirchhoff has shown that

$$u = A_Q - A_1 m (h/\lambda_1 - v) Q_1 - A_2 m (h/\lambda_2 - v) Q_2 \quad \dots\dots(24),$$

$$s = -A \cdot \frac{m}{h/\mu - m^2} \frac{dQ}{dr} - A_1 \left(\frac{h}{\lambda_1} - v \right) \frac{dQ_1}{dr} - A_2 \left(\frac{h}{\lambda_2} - v \right) \frac{dQ_2}{dr} \quad \dots\dots(25),$$

$$\theta = A_1 Q_1 + A_2 Q_2 \quad \dots\dots(26),$$

 u, s θ δT a μ, v λ_1, λ_2

where u and s are the longitudinal and radial velocity components respectively, and θ is proportional to the temperature-difference between the actual state and the undisturbed state, and is defined by $\theta = \delta T \cdot a / (\gamma - 1)$, where δT is this temperature-difference, and a is defined by $p \rho = p_0 \rho_0 \cdot (1 - a \cdot \delta T)$, so that for a perfect gas $\theta = T^{-1} \delta T / (\gamma - 1)$. μ and v are equal to η/ρ and $k/c_p \rho$ respectively, and are thus measures of the viscosity and thermal conductivity. λ_1 and λ_2 are the roots of the equation

$$h^2 - \{a^2 + h(4\mu/3 + v)\} \lambda + v/h \cdot \{b^2 + h \cdot 4\mu/3\} \lambda^2 = 0 \quad \dots\dots(27),$$

 a, b

where a and b are defined by $\sqrt{(p_0 \rho_0 \cdot \gamma)}$ and $\sqrt{(p_0 \rho_0)}$ respectively, so that for a perfect gas they are equal to the adiabatic and isothermal sound-velocities respectively.

 Q, Q_1, Q_2

Q , Q_1 , and Q_2 are functions of r which satisfy the following equations:

$$\frac{d^2 Q}{dr^2} + \frac{1}{r} \cdot \frac{dQ}{dr} - (h/\mu - m^2) Q = 0 \quad \dots\dots(28).$$

$$\frac{d^2 Q_1}{dr^2} + \frac{1}{r} \cdot \frac{dQ_1}{dr} - (\lambda_1 - m^2) Q_1 = 0 \quad \dots\dots(28).$$

$$\frac{d^2 Q_2}{dr^2} + \frac{1}{r} \cdot \frac{dQ_2}{dr} - (\lambda_2 - m^2) Q_2 = 0 \quad \dots\dots(28).$$

 A, A_1, A_2

A , A_1 , and A_2 are constants to be determined by the boundary conditions. Apparently, the only approximations which have been made in deducing the above equations are the assumption of small amplitude, and that u , s , and θ vary as $e^{i\omega t}$. Lord Rayleigh⁽²¹⁾ has shown that in a Kundt's tube there are actually continuous circulations between the nodes and antinodes, but these depend upon small quantities of the second order, which for our present purpose we can neglect.

Kirchhoff determined the velocity of sound in the tube on his assumptions by putting u , s , and θ all equal to zero when $r = R$ and eliminating the A 's from the resulting equations. We shall allow for various factors by putting the appropriate values for u , s , and θ when $r = R$ and then proceeding as before. In order to avoid complications we shall not allow for all the factors at once, but shall take them one by one. Since it will appear that the corrections thus introduced are all very small, we may suppose that any combination terms which would appear if we allowed for all the factors at once will be still smaller and may be neglected.

(ii) *The effect of slip.* To allow for this we will make use of Maxwell's expression and put $u = -\omega(\partial u/\partial r)_{r=R}$ at the boundary, where

$$\omega = \eta\sqrt{(\pi/2)p_0\rho_0)} \cdot (2-f)/f \quad \dots\dots(29), \quad \omega$$

f being the fraction of the molecules which is diffusely reflected on striking the wall.

Substituting in equation (24) we get, when $r = R$,

$$A(Q + \omega dQ/dr) - A_1 m(h/\lambda_1 - \nu)(Q_1 + \omega dQ_1/dr) - A_2 m(h/\lambda_2 - \nu)(Q_2 + \omega dQ_2/dr) = 0 \dots\dots(30).$$

Putting $s = 0$, $\theta = 0$ when $r = R$ in equations (25) and (26), and eliminating the A 's, we get

$$\left| \begin{array}{ccc} 0 & Q_1 & Q_2 \\ -(Q + \omega dQ/dr) & m(h/\lambda_1 - \nu)(Q_1 + \omega dQ_1/dr) & m(h/\lambda_2 - \nu)(Q_2 + \omega dQ_2/dr) \\ \frac{m}{h/\mu - m^2} \frac{dQ}{dr} & \left(\frac{h}{\lambda_1} - \nu\right) \frac{dQ_1}{dr} & \left(\frac{h}{\lambda_2} - \nu\right) \frac{dQ_2}{dr} \end{array} \right| = 0 \dots\dots(31).$$

After multiplying out and dividing through by QQ_1Q_2 , we now approximate, as did Kirchhoff, by putting

$$\begin{aligned} d \log Q/dr &= \sqrt{(h/\mu)}; \quad d \log Q_1/dr = r(\lambda_1 - m^2)/2; \\ d \log Q_2/dr &= \sqrt{\lambda_2}; \quad \lambda_1 = h^2/a^2; \quad \lambda_2 = ha^2/vb^2 \end{aligned}$$

and in the term containing $\sqrt{\mu}$, $m = h/a$. See Kirchhoff's paper for the justification of these. We thus get

$$m^2 = h^2/a^2 \cdot (1 + 2\delta/R\sqrt{h}) \dots\dots(32),$$

where $\delta = \sqrt{\mu} \{1 + \omega\sqrt{(h/\mu)}\}^{-1} + (a/b - b/a)\sqrt{\nu}$. δ

Putting $h = 2\pi ni$, separating out the real and imaginary parts and neglecting the square of the quantity $\omega\sqrt{(\pi n/\mu)}$ which with actual gases is small, we get

$$m = \pm \left[\frac{\sqrt{(\pi n)}}{aR} \left\{ \sqrt{\mu} + \left(\frac{a}{b} - \frac{b}{a}\right) \sqrt{\nu} \right\} + i \left\{ \frac{2\pi n}{a} + \frac{\sqrt{(\pi n)}}{aR} \left(\frac{\sqrt{\mu}}{1 + 2\omega\sqrt{(\pi n/\mu)}} + \left(\frac{a}{b} - \frac{b}{a}\right) \sqrt{\nu} \right) \right\} \right] \dots\dots(33),$$

so that if $m = m' + im''$, we have

$$\begin{aligned} \text{Sound-velocity} &= 2\pi n/m'' \\ &= a \{1 - \beta_1/2R\sqrt{(\pi n)}\}, \end{aligned}$$

$$\text{where } \beta_1 = \frac{\sqrt{\mu}}{1 + \pi \{(2-f)/f\}\sqrt{(2n\eta/p)}} + \left(\frac{a}{b} - \frac{b}{a}\right) \sqrt{\nu} \quad \dots\dots(34). \quad \beta_1$$

(iii) *The effect of radial motion at the walls.* This includes both the yielding of the tube walls, and, as explained on page 343, the absorption of energy by the walls. Let us suppose that at the walls $s = \chi(p - p_0)/p_0$, where χ is complex. Let σ be the condensation at any point, so that $\rho = \rho_0(1 + \sigma)$. Then it follows from the definitions of σ and θ that

$$p - p_0 = p_0\sigma + p_0(\gamma - 1)\theta.$$

Therefore $(p - p_0)/p_0 = \sigma + (\gamma - 1)\theta$
 $= \gamma\theta - \nu\Delta\theta/h,$

where $\Delta\theta = \partial^2\theta/\partial x^2 + \partial^2\theta/\partial y^2 + \partial^2\theta/\partial z^2,$

therefore $(p - p_0)/p_0 = \gamma\theta - (A_1\lambda_1 Q_1 + A_2\lambda_2 Q_2).\nu/h$
 $= A_1(\gamma - \nu\lambda_1/h)Q_1 + A_2(\gamma - \nu\lambda_2/h)Q_2 \quad \dots\dots(35).$

See Kirchhoff's paper for the derivations of the relations on which these rest.

Hence, putting $s = \chi(p - p_0)/p_0$ when $r = R$ in equation (25), and $u = 0$ and $\theta = 0$ when $r = R$ in equations (24) and (26), and eliminating the A 's, we get

$$\begin{array}{c} \text{o} & Q_1 & Q_2 & = \text{o} \\ \hline \frac{m}{h/\mu - m^2} \frac{dQ}{dr} & \left(\frac{h}{\lambda_1} - \nu\right) \frac{dQ_1}{dr} + \chi \left(\gamma - \frac{\nu\lambda_1}{h}\right) Q_1 & \left(\frac{h}{\lambda_2} - \nu\right) \frac{dQ_2}{dr} + \chi \left(\gamma - \frac{\nu\lambda_2}{h}\right) Q_2 \\ Q & - m(h/\lambda_1 - \nu) Q_1 & - m(h/\lambda_2 - \nu) Q_2 \\ \hline & & & \dots\dots(36). \end{array}$$

This after a little simplification and division by $Q_1 Q_2 Q$ gives

$$\frac{m^2 h}{h/\mu - m^2} \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right) \frac{d \log Q}{dr} + \left(\frac{h}{\lambda_1} - \nu\right) \frac{d \log Q_1}{dr} - \left(\frac{h}{\lambda_2} - \nu\right) \frac{d \log Q_2}{dr} - \chi \frac{\nu}{h} (\lambda_1 - \lambda_2) = 0 \quad \dots\dots(37),$$

and with the same approximations as before, this gives:

$$m^2 = \frac{h^2}{a^2} \left[1 + \frac{2}{R} \left\{ \frac{\beta}{\sqrt{h}} + \chi \left(\frac{1}{h} \frac{a^2}{b^2} - \frac{\nu}{a^2} \right) \right\} \right].$$

χ' , χ'' Putting $h = 2\pi n i$, so that $\sqrt{(1/h)} = (1-i)/2\sqrt{(\pi n)}$ and $\chi = \chi' + i\chi''$, we get

$$m^2 = \frac{4\pi^2 n^2}{a^2} \left[1 + \frac{1}{R} \left\{ \frac{\beta}{\sqrt{(\pi n)}} + \frac{\gamma\chi''}{\pi n} - \frac{2i\chi'}{a^2} \right\} - \frac{i}{R} \left\{ \frac{\beta}{\sqrt{(\pi n)}} + \frac{\gamma\chi'}{\pi n} - \frac{2i\chi''}{a^2} \right\} \right].$$

Now if x and y are small

$$\sqrt{(-1 - x + iy)} = (-\frac{1}{2}y + \frac{1}{4}xy) + i(1 + x + \frac{1}{4}y^2) \text{ nearly,}$$

so that if we neglect squares of β and ν and the cubes, etc. of χ' and χ'' , and if $m = m' + im''$, we get

$$\left. \begin{aligned} m' &= \frac{\sqrt{(\pi n)}}{aR} \beta + \frac{\gamma}{aR} \chi' + \frac{2\pi n}{a^3 R} \nu \chi'' - \frac{\gamma^2}{2aR^2 \pi n} \chi' \chi'' \\ m'' &= \frac{2\pi n}{a} + \frac{\sqrt{(\pi n)}}{aR} \beta + \frac{\gamma}{aR} \chi'' - \frac{2\pi n}{a^3 R} \nu \chi' + \frac{\gamma^2}{4aR^2 \pi n} (\chi'^2 - \chi''^2) \end{aligned} \right\} \dots\dots(38).$$

\therefore Sound-velocity = $2\pi n/m''$

$$= a \left\{ 1 - \frac{\beta}{2R\sqrt{(\pi n)}} - \frac{\gamma}{2\pi n R} \chi'' + \frac{\nu\chi'}{a^2 R} + \left(\frac{\gamma}{R\pi n} \right)^2 \frac{2\chi''^2 - \chi'^2}{8} \right\} \dots\dots(39).$$

The term in χ'' is the correction for the elastic yielding of the tube, and if we put $\chi'' = 2\pi n R^2 p_0 / II\tau$ it becomes $\gamma p R / II\tau$, which is identical with the expression

obtained by Lamb. We have already seen (p. 343) that it can be neglected. Hence we may also neglect the term in χ''^2 , and write

$$\text{Sound-velocity} = a \left\{ 1 - \frac{\beta}{2R\sqrt{(\pi n)}} + \frac{\nu\chi'}{a^2 R} - \left(\frac{\gamma}{R\pi n} \right)^2 \frac{\chi'^2}{8} \right\} \dots\dots(40).$$

The amplitude of a progressive wave diminishes as it goes along the tube proportionally to $e^{-m'x}$; and since the terms in χ'' can be shown to be negligible we may write

$$m' = \{\beta\sqrt{(\pi n)} + \gamma\chi'\}/aR \dots\dots(41).$$

(iv) *The effects of the temperature discontinuity* at the surface of the tube, and of the *finite conductivity* of the tube wall may conveniently be treated together. Let ϕ be the temperature, reckoned from the mean, at a point in the material of the tube at a distance z from the inner surface, and let κ , ρ_t , and c be the thermal conductivity, the density, and specific heat per gramme of the tube material. At the frequencies used in practice the changes of temperature due to the vibrations of the gas will only penetrate a short distance into the tube wall, and we shall not introduce any appreciable error if we consider the surface to be plane instead of cylindrical. We then have

$$\frac{\partial^2 \phi}{\partial z^2} = \frac{\rho_t c}{\kappa} \frac{\partial \phi}{\partial t}.$$

We may assume that $\phi \propto e^{ht}$, and we get as the solution for which $\phi = 0$ when $z = \infty$, and $\phi = \phi_0 = \Phi_0 e^{ht}$ when $z = 0$

$$\phi = \phi_0 \cdot \exp \{-\sqrt{(\pi n \rho_t c / \kappa)} z\} \dots\dots(42),$$

or, taking the real part,

$$\phi = \Phi_0 \cdot \exp \{-\sqrt{(\pi n \rho_t c / \kappa)} z\} \cdot \cos 2\pi n \{t - \sqrt{(\rho_t c / 4\pi n \kappa)} z\} \dots\dots(43).$$

This represents a system of waves whose amplitude decreases to $1/e$ times its initial value in a distance which, for glass, is about 7×10^{-4} cm.; so that our assumption of a plane surface instead of a cylindrical was quite justifiable.

The rate at which heat crosses unit area of the inner surface of the tube is given by

$$-\kappa (\partial \phi / \partial z)_{z=0} = \sqrt{(h \rho_t c \kappa)} \phi_0,$$

and this must be equal to

$$\zeta (\delta T - \phi_0) = \zeta \{(\gamma - 1) \theta / \alpha - \phi_0\},$$

where ζ is the thermal permeability of the interface; and also to

$$-k \cdot \partial T / \partial r = -k (\gamma - 1) / \alpha \cdot \{A_1 \cdot dQ_1 / dr + A_2 \cdot dQ_2 / dr\}.$$

Eliminating ϕ_0 between these three equal quantities, we get

$$\begin{aligned} -k \left(A_1 \frac{dQ_1}{dr} + A_2 \frac{dQ_2}{dr} \right) &= \frac{\sqrt{(\rho_t c \kappa h)}}{\sqrt{(\rho_t c \kappa h)} + \zeta} \cdot \zeta \theta \\ &= \psi (A_1 Q_1 + A_2 Q_2) \end{aligned}$$

by equation (26), where

$$\psi^{-1} = (\rho_t c \kappa h)^{-1} + \zeta^{-1}.$$

Hence when $r = R$

$$A_1 \left\{ Q_1 + \frac{k}{\psi} \frac{dQ_1}{dr} \right\} + A_2 \left\{ Q_2 + \frac{k}{\psi} \frac{dQ_2}{dr} \right\} = 0 \dots\dots(44).$$

Putting $u = 0$ and $s = 0$ when $r = R$ in equations (24) and (25), and eliminating the A 's, we have

$$\left| \begin{array}{l} 0 \quad Q_1 - \frac{k}{\psi} \frac{dQ_1}{dr} \quad Q_2 - \frac{k}{\psi} \frac{dQ_2}{dr} = 0 \\ Q \quad -m \left(\frac{h}{\lambda_1} - v \right) Q_1 - m \left(\frac{h}{\lambda_2} - v \right) Q_2 \\ -\frac{m}{h/\mu - m^2} \frac{dQ}{dr} - \left(\frac{h}{\lambda_1} - v \right) \frac{dQ_1}{dr} - \left(\frac{h}{\lambda_2} - v \right) \frac{dQ_2}{dr} \end{array} \right. \dots\dots(45).$$

Simplifying this, dividing by $Q_1 Q_2$ and making the usual approximations, we get

$$m^2 = h^2/a^2 \cdot (1 + 2\epsilon/R\sqrt{h}),$$

$$\epsilon = \sqrt{\mu} + \frac{(a/b - b/a)\sqrt{v}}{1 + (ka/\psi b)\sqrt{(h/v)}}.$$

Putting $h = 2\pi ni$ so that $\sqrt{h} = \sqrt{(\pi n)}(1 + i)$ and $m = m' + im''$, we finally get

$$\epsilon = \sqrt{\mu} - \frac{(a/b - b/a)\sqrt{v}}{1 - \sqrt{(\rho c_p k/\rho_t c_\nu)} - \sqrt{(\pi n k c_p/\rho_t)}(1 - i)/\zeta},$$

and

$$m = \pm \{\sqrt{(\pi n)}\epsilon/aR + i(2\pi n/a + \sqrt{(\pi n)}\epsilon/aR)\},$$

from which we get

$$\left. \begin{array}{l} m' = \frac{\sqrt{(\pi n)}}{aR} \left\{ \sqrt{\mu} \pm \frac{(a/b - b/a)\sqrt{v}}{1 + \omega_1 + \omega_2} \right\} \\ m'' = \frac{2\pi n}{a} + \frac{\sqrt{(\pi n)}}{aR} \left\{ \sqrt{\mu} + \frac{(a/b - b/a)\sqrt{v}}{1 + \omega_1 + 3\omega_2} \right\} \end{array} \right\} \dots\dots(46),$$

ω_1 where

$$\omega_1 = \sqrt{(k\rho c_p/\kappa \rho_t c)},$$

ω_2 and

$$\omega_2 = \sqrt{(\pi n k \rho c_p)/\zeta},$$

so that

$$\text{Sound-velocity} = 2\pi n/m''$$

$$= a \{1 - \beta_2/2R\sqrt{(\pi n)}\} \dots\dots(47),$$

β_2 where

$$\beta_2 = \sqrt{\mu} + \frac{(a/b - b/a)\sqrt{v}}{1 + \omega_1 + 3\omega_2}.$$

The expressions (7) and (8) on pp. 344, 345, are obtained by putting $\omega_1 = 0$ and $\omega_2 = 0$ respectively.

(v) *The effect of vibrations of the stop.* Let x denote the distance of any point along the tube from the stop. Let the particle-velocity of the gas in the tube be given by

$$u = c_1 e^{mx+ht} + c_2 e^{-mx+ht} \dots\dots(48),$$

where c_1, c_2 and m may be complex, and $h = 2\pi ni$.

Then if the stop vibrates so that its velocity is given by

u_0, c

$$u_0 = ce^{ht} \dots\dots(49),$$

we must have

$$c_1 + c_2 = c,$$

and

$$u = \{c_1 e^{mx} + (c - c_1) e^{-mx}\} e^{ht} \dots\dots(50).$$

The motion of the stop is produced by the changes of pressure on it. Let it be given by

$$u_0 = Dp_0 \quad \dots\dots(51), \quad D, p_0$$

where D may be complex.

Now if p be the excess pressure in the gas over the mean, due to the vibrations, we have

$$p = -(Em/h) \{c_1 e^{mx} - (c - c_1) e^{-mx}\} e^{ht},$$

$$\text{and when } x = 0 \quad p_0 = -(Em/h) (2c - c_1) e^{ht} \quad \dots\dots(52),$$

where E is the elasticity of the gas.

From equations (49), (51) and (52) we get

$$c = -(DEM/h) (2c - c_1),$$

$$\text{so that } c_1 (1 + h/DEM) (1 - h/DEM)^{-1} = -c (1 + 2DEM/h)$$

nearly, if DEM/h is small.

Thus, substituting in equation (50), we get

$$u = c_1 \{e^{mx} - (1 + 2DEM/h) e^{-mx}\} e^{ht} \quad \dots\dots(53).$$

If we neglect the damping effect of the tube on the gas vibrations, we can put $m = 2\pi i/\lambda$. Also $h = 2\pi ni$, so that

$$h/m = n\lambda = a = \sqrt{(E/\rho)};$$

and

$$Em/h = \sqrt{(E\rho)}.$$

Let us also put $D = D' + iD''$, and take the real part of equation (53). We thus get for the velocity-amplitude at any point

$$|u| = 2c_1 \sqrt{E\rho} (D'^2 + D''^2) \\ + \{\sin 2\pi x/\lambda - 2\sqrt{(E\rho)} \cdot D'' \cos 2\pi x/\lambda\} \{1 + 2\sqrt{(E\rho)} D'\} \sin 2\pi x/\lambda \dots(54),$$

and this gives for the positions of the nodes and antinodes

$$\tan 4\pi x/\lambda = 2\sqrt{(E\rho)} D'' \quad \dots\dots(55).$$

Turning our attention now to the piston-rod, let us denote by l the distance between the point at which it is clamped and the piston. Then if H and ρ_1 be the Young's modulus and density of the rod, and we now measure distances from the clamped point, we can assume for the motion of the rod (if we neglect the mass of the piston)

$$u_1 = B (e^{m_1 x} - e^{-m_1 x}) e^{ht} \quad \dots\dots(56), \quad m_1$$

$$\text{and also } p_1 = -(l\rho_1 B/m_1) (e^{m_1 x} + e^{-m_1 x}) e^{ht} \quad \dots\dots(57). \quad \rho_1$$

Since the damping of the motion of the rod will be found to be important, we cannot now assume that m_1 is entirely imaginary, but write $m_1 = m_1' + im_1''$. At the piston we have $x = l$, and $p_1 = p_0 \cdot A_p/A_r$, where A_p and A_r are the areas of cross-section of the piston and rod respectively, and p_0 is the gas pressure. Also $u_1 = u_0$ and hence

$$D' + iD'' = u_0/p_0 \\ - \frac{m_1' + im_1''}{h\rho_1} \frac{e^{m_1 l} - e^{-m_1 l} A_p}{e^{m_1 l} + e^{-m_1 l} A_r} \quad \dots\dots(58).$$

Putting $h = 2\pi ni$; separating real and imaginary parts, and equating the latter, we get

$$D'' = \frac{1}{2\pi n\rho_1} \cdot \frac{A_p}{A_r} \cdot \frac{m_1' \sinh 2m_1' l - m_1'' \sin 2m_1'' l}{\cosh 2m_1' l + \cos 2m_1'' l} \quad \dots\dots(59).$$

Putting $2\pi n/m'' = \sqrt{(H/\rho)}$; $m'' = 2\pi/\lambda'$; $m' = 1/\mu$,

and (since $m_1'l'$ is small)

$$\sinh 2m_1' l = 2m_1' l$$

and

$$\cosh 2m_1' l = 1 + 2m_1'^2 l^2;$$

we get

$$D'' = \frac{1}{\sqrt{(\rho_1 H)}} \cdot \frac{A_p}{A_r} \cdot \frac{(\lambda' l / \pi \mu^2) - \sin (4\pi l / \lambda')}{(l^2 / \mu^2) + \cos^2 (2\pi l / \lambda')} \quad \dots\dots(60).$$

Combining equations (55) and (60) we get for the positions of the nodes and anti-nodes in the gas

$$\tan (4\pi x / \lambda) = \sqrt{\left(\frac{\rho E}{\rho_1 H}\right) \cdot \frac{A_p}{A_r} \cdot \frac{(\lambda' l / \pi \mu^2) - \sin (4\pi l / \lambda')}{(l^2 / \mu^2) + \cos^2 (2\pi l / \lambda')}} \quad \dots\dots(61).$$

(vi) *The effect of the gap between the piston and tube wall.* Irons⁽²²⁾ has recently published two papers on the effect of constrictions in a Kundt's tube, in which he shows both theoretically and experimentally, that if an aperture of acoustical conductance c divides a tube of cross-sectional area s into two parts, and if l_1 and l_2 be the distances from the aperture to the nodes on either side of it, then

$$\cot (2\pi l_1 / \lambda) + \cot (2\pi l_2 / \lambda) = 2\pi s / \lambda c \quad \dots\dots(62).$$

If the length of the tube, or the position of the aperture, is adjusted for resonance, the distances of the ends of the tube from the aperture will be connected by this equation.

If, owing to the presence of the piston-rod on one side, the cross-sectional areas and the wave-lengths are different on the two sides, we must write, when the piston is adjusted for resonance,

$$s_1^{-1} \cdot \cot (2\pi l / \lambda_1) + s_2^{-1} \cdot \cot \{2\pi (L - l) / \lambda_2\} = 2\pi / \lambda_1 c \quad \dots\dots(63),$$

L, l

where L is the total length of the tube, l is the length of the portion not containing the piston-rod. If the piston-rod end of the tube is open instead of being closed by a gland, we merely substitute a minus sign for the plus in the above equation. This equation, if solved for l , gives the various resonance positions of the piston. I have not obtained an exact solution, but we can get an approximate solution as follows:

L'

Let $\lambda_2 = \lambda_1 (1 - \alpha)$, and $L' = L + (L - l) \alpha$; and $\mathcal{R} = s_1/s_2$. Equation (63) now becomes

$$\cot (2\pi l / \lambda_1) + \mathcal{R} \cot \{2\pi (L' - l) / \lambda_1\} = 2\pi s_1 / \lambda_1 c = B \text{ (say)} \quad \dots\dots(64).$$

We can think of L' as the effective length of the tube; i.e. the length which would give resonance with the same value of l , if the velocity were the same in both parts of the tube. It is a quantity which varies slowly with the position of the piston, for α may be of the order 0.002. L' is equal to L when the piston is right out, and in other positions

$$L' - L = \alpha (L - l) \quad \dots\dots(65).$$

B

Hence the shift in the position of the nodes relative to the piston, due to the sound-velocity behind the piston not being equal to that in front (i.e. due to the effective tube length being L' instead of L), is given by

$$\alpha(L - l) \cdot dl/dL' \text{ approximately} \quad \dots\dots(66).$$

Where dl/dL' is obtained by differentiating equation (64) not from (65).

Now one of the nodes is at the source of the sound when the piston is adjusted for resonance, and hence the above expression is equal to the shift in the resonance position of the piston due to the inequality of the sound-velocities on the two sides of the piston.

If these velocities were equal, equation (62) would hold for the resonance positions, and it is readily seen that in this case the distance between successive positions is exactly equal to λ . From this it follows that, in the actual case, the error in measuring this distance is equal to

$$\alpha(L - l_1)(dl/dL')_1 - \alpha(L - l_2)(dl/dL')_2 \quad \dots\dots(66).$$

Now $l_1 - l_2$ is nearly equal to λ_1 ; and it will shortly be shown that $(dl/dL')_1$ and $(dl/dL')_2$ are very nearly equal. Thus the error in λ is

$$-\alpha \cdot dl/dL',$$

and the fractional error is $-\alpha\lambda_1 \cdot dl/dL'$ $\dots\dots(67)$.

Differentiating equation (64) we get

$$[s_2^{-1} \cdot \operatorname{cosec}^2 \{2\pi(L' - l)/\lambda_1\} - s_1^{-1} \cdot \operatorname{cosec}^2 \{2\pi l/\lambda_1\}] dl - [s_2^{-1} \cdot \operatorname{cosec}^2 \{2\pi(L' - l)/\lambda_1\}] dL' = 0.$$

$$\begin{aligned} \text{Hence } dL'/dl &= 1 - \mathcal{R}^{-1} \cdot \{1 + \cot^2(2\pi l/\lambda_1)\} \sin^2 \{2\pi(L' - l)/\lambda_1\} \\ &= 1 - \mathcal{R}^{-1} \cdot \{1 + (B - \mathcal{R} \cot \theta)^2\} \sin^2 \theta, \end{aligned}$$

$$\text{where } \theta = 2\pi(L' - l)/\lambda_1,$$

$$\text{and } dL'/dl = \frac{1}{2}(2 - \mathcal{R} - 1/\mathcal{R} - B^2/\mathcal{R}) - \frac{1}{2}(\mathcal{R} - 1/\mathcal{R} - B^2/\mathcal{R}) \cos 2\theta + B \sin 2\theta \quad \dots\dots(68).$$

If the piston-rod is small compared with the tube, so that \mathcal{R} is not far from unity; and if B^2/\mathcal{R} is considerably greater than unity, we can write this

$$dL'/dl = B \{\sin 2\theta - B \sin^2 \theta\} \quad \dots\dots(69).$$

$$\text{Now } \theta = 2\pi(L' - l)/\lambda_1 = 2\pi(1 + \alpha)(L - l)/\lambda_1,$$

and since α is of the order 0.002 (in the case of Partington and Shilling's silica apparatus), and $l = \frac{1}{2}N\lambda_1$ approximately at the resonance positions, θ will be approximately equal to $2\pi(1 + \alpha)L/\lambda_1 - \pi N$; and dL'/dl will be nearly the same for all the resonance positions and roughly will be dependent on L/λ_1 only. This will be a good approximation for the conditions when the effect of the coupling is small, whilst if the tube length is such that the effect is large we must apply $\theta = 2\pi(L' - l)/\lambda_1$ separately for each position of the piston in the tube. On these assumptions, we get

$$\text{Proportional error in velocity} = \alpha/B(B \sin^2 \theta - \sin 2\theta) \quad \dots\dots(70).$$

(vii) *The yielding of a tube of elliptical cross-section.* Rayleigh⁽²³⁾ gives for the frequency of vibration of an inextensible elastic circular ring a formula which for the lowest mode, becomes $n = (3t/\pi R^2)\sqrt{(H/60\rho)}$ (71),

after the appropriate substitutions have been made (and a misprint corrected). Here t is the wall thickness, ρ the density of the material, and H the Young's modulus. For a silica tube of diameter 2·5 cm., and wall thickness 3 mm. this gives a frequency of about 8000 ~. We shall assume that the sound vibrations have a considerably lower frequency than this, so that the displacements of the tube wall will have the same values as they would have if the same pressures were applied statically. Consider a thin ring of the tube contained between two planes perpendicular to the axis of the tube and at a distance δx apart. Let the minor and major axes of the ellipse be $2a$ and $2b$ respectively. We shall suppose the wall to be thin compared with a or b and we shall define positions on the ellipse by means of the eccentric angle ϕ , reckoned as zero at an extremity of the minor axis. Let $M_\phi \cdot \delta x$ be the bending moment at the position ϕ ; and p be the excess pressure on the inside due to the sound waves.

The resultant of this pressure on one quarter-arc of the ellipse must be identical with that which the same pressure would exert on the arc joining the extremities of the quadrant, by a well known theorem in hydrostatics. Hence, taking moments about an extremity of the minor axis, of the forces on the quadrant we get

$$M_\phi = M_0 + \frac{1}{2}p(b^2 - a^2) \sin^2 \phi \quad \dots\dots(72).$$

Let $U \cdot \delta x$ be the total potential energy of bending of the ring.

Then

$$U = \oint \frac{1}{2}M^2/P ds$$

round the ellipse; where $P = Ht^3/12$ and H and t are the Young's modulus and thickness of the tube walls.

Therefore

$$U = \frac{2}{P} \int_0^l M^2 ds,$$

where l is the length of a quadrant,

$$= \frac{2M_0^2 l}{P} + \frac{2p(b^2 - a^2)}{P} \int_0^{\pi/2} \{M_0 \sin^2 \phi + \frac{1}{2}p(b^2 - a^2) \sin^4 \phi\} b \sqrt{(1 - e^2 \sin^2 \phi)} d\phi, \\ (\text{where } e^2 = 1 - a^2/b^2)$$

$$= 2P^{-1} \cdot \{M_0^2 l + M_0 p e^2 b^3 \cdot \frac{1}{4}\pi (1 - \frac{3}{8}e^2) + (3\pi/64) p^2 e^4 b^5\}$$

nearly, if e is small. If $a/b = 4/5$ the error is less than 2 per cent.

Therefore

$$U = 2p^2 b^5 P^{-1} \cdot \{\beta^2 E f^4 - \beta f^2 \cdot \frac{1}{4}\pi (1 - f^2) (\frac{5}{8} + \frac{3}{8}f^2) + (3\pi/64) (1 - f^2)^2 (7/12 - 5f^2/12)\},$$

where M_0 has been given its value $\beta p a^{2*}$; f has been written for $a/b = \sqrt{(1 - e^2)}$ and E is an elliptic integral of the second kind giving the ratio l to b .

Now U must also be equal to $\frac{1}{2}p \cdot \delta s$, where δs is the increase in area.

Therefore

$$\delta s/s = 2U/p s$$

$$= (4b^3 p / P \pi f) \cdot \{ \dots \},$$

since

$$s = \pi b^2 f.$$

* See Timoshenko's *Elasticity*, p. 242.

If we consider a slice of gas extending across the tube and of volume $s \cdot \delta x$ when undisplaced, its volume when displaced is $(s + \delta s)(1 + \partial \xi / \partial x) \delta x$, which is nearly equal to $s \cdot \delta x(1 + \partial \xi / \partial x + \delta s / s)$.

Hence if E is the elasticity of the gas, we have

$$p = -E \cdot \delta v / v = -E [\partial \xi / \partial x + (4b^3 / P\pi f) \cdot p \{ \dots \}],$$

and hence $p = -E (\partial \xi / \partial x) [1 + (4b^3 / P\pi f) \cdot \{ \dots \}]^{-1}$,

i.e. the elasticity has apparently been decreased by the fraction

$$(4b^3 / P\pi f) \{ \dots \}.$$

Hence the sound-velocity is decreased by a fraction

$$(\gamma p \epsilon / H) \cdot (b/t)^3,$$

where

$$\epsilon = 2f^{-1} \{ 12\pi^{-1} \beta^2 Ef^4 - \frac{3}{8} \beta f^2 (1 - f^2) (5 + 3f^2) + 3/64 \cdot (1 - f^2)^2 (7 + 5f^2) \} \dots \quad (73).$$

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DISCUSSION

Dr E. G. RICHARDSON. With regard to the possibility of irregular motion, and its influence on the propagation of sound in a tube, I would like to point out that owing to the annular effect the amplitude of vibration of the particles may be greater near the walls of the tube than at the centre. The position of the peak amplitude is in fact determined by the very factor quoted by Mr Henry: i.e. the distance of the maximum amplitude from the walls is proportional to $\sqrt{(\mu n)}$. The excrescences on the surface referred to by the author are therefore likely to project into a region where there is a steep gradient of particle-velocity, instead of into comparatively still air. Will not this fact alone, by encouraging irregular motion, invalidate the premises of the Kirchhoff formula?

AUTHOR's reply. I am much indebted to Dr Richardson for pointing out that the velocity-gradient near the walls may be much greater than that given by the simple theory on which my statement on p. 345 was based. The effect he describes should very much reduce the size of the irregularities required to produce unordered motion. Thus if we make use of the theory given in the paper of Richardson and Tyler* and assume a frequency of 3000 ~ in air we find that the velocity has a maximum amplitude 1.07 times that at the centre of the tube at a distance of only about 0.1 mm. from the wall. The theory would probably be upset by the closed ends of the tubes used in practice, but the gap between the piston and the walls at one end would probably accentuate the effect near that end at least. It would be interesting to see whether the form of the piston and telephone receiver affect the tube-effect in this way.

Mr W. LUCAS referred to the sentence following equation (21) in which the author states that diameter-errors will cancel out if the nodal distances be measured in the best way. Would the author state what is the best way?

AUTHOR's reply. The way I had in mind is to find the positions of, say, twenty nodes, to take the mean of the distances between the first and eleventh, the second and twelfth, the third and thirteenth, and so on; and to divide this by ten. This method gives equal weight to all the observations, instead of giving one observation the same weight as all the rest put together.

* *Proc. Phys. Soc.* **42**, 1 (1929).

DEMONSTRATION

Some elementary experiments concerned with sound-waves in tubes. *Demonstration given on March 6, 1931*, by ERIC J. IRONS, Ph.D.

The following experiments and slides were shown:

1. Mechanical lantern slide to demonstrate the formation and properties of stationary waves. The slide consists of two chemically fixed photographic plates upon each of which a sine curve is drawn. Means are provided whereby the curves move in opposite directions and the resultant displacements for various positions of the waves are registered on the board upon which the slide is focussed.
2. Five lantern slides* illustrating the formation of dust figures in a Kundt's tube excited by a rod.
3. Determination of the end-correction of a tube. Dust figures give an ocular demonstration of the fact that an antinode is not formed exactly at the open end of a Kundt's tube and enable an estimate of the end-correction to be made.†
4. Demonstration of the effect of a Quincke filter on the sound emitted from a valve-maintained tube. If a side branch tuned to a note of a particular frequency is fixed in a conduit down which sound-waves are passing, the energy associated with that frequency is absorbed in the branch.

* *Phil. Mag.* 7, 523 (1929).

† *Phil. Mag.* 6, 580 (1928).

REVIEWS OF BOOKS

Tables Annuelles de Constantes et Données Numériques. Vol. 7, Pt 2. Pp. xv + 950.
(Paris, Gauthier-Villars et Cie.)

Earlier parts of this series of scientific tables have been favourably mentioned in these columns previously. A complete set comprises seven volumes, which must be bought as a whole, and for which the price of subscription is 84 dollars.

The present volume 7 gives data for the years 1925-26. Notes and descriptive portions belonging to the various tables are given in French and English. The matter dealt with includes subjects of an electrical nature such as ionization, thermions, radioactivity, isotopes, but also organic chemistry and subjects such as the properties of materials, which border on engineering. The book is very clearly printed and well produced. It is interesting to note that an index to volumes 1 to 5 is to appear, a very unexpected but acceptable feature in a French book.

J. E. C.

Standard Four-Figure Mathematical Tables, by L. M. MILNE-THOMSON, M.A. and L. J. COMRIE, M.A., Ph.D. Pp. xvi + 245. (London: Macmillan and Co., Ltd.) 10s. 6d.

This is a very useful collection of mathematical tables and formulae which are of very frequent application. Several features of interest may be mentioned.

Although the logarithms are given to only four figures, differences are printed at the side of a column, and to secure greater accuracy than that obtained by the usual method of interpolation, the following device is used. A dot if placed high after the fourth figure indicates that - 3 occurs in the next place, and if placed low may be taken to represent - 3 in the fifth place. Thus when several members are multiplied together a little additional accuracy is obtained.

A good feature of the tables is that on some pages are given no fewer than ten functions such as $\sin x$, $\cot x$, $\log \sin x$, $\log \cos x$, etc. Natural logarithms, hyperbolic functions, gamma functions, roots and reciprocals are included. The latter part of the book is devoted to lists of integrals, series, mensuration formulae and other similar information. One has rather a suspicion that a reader using some of the more advanced tables would require logarithms of greater accuracy than that given by four figures, but nevertheless the book may be strongly recommended.

J. E. C.

National Physical Laboratory Collected Researches. Vol. 21, 1929. Pp. iv + 448.
(London: H.M. Stationery Office.) 22s. 6d.

National Physical Laboratory Collected Researches. Vol. 22, 1930. Pp. iv + 417.
(London: H.M. Stationery Office.) 20s.

The twenty-first and twenty-second volumes of the collected researches of the National Physical Laboratory show an impressive record of work put out by the members of the Electricity Department. As is to be expected, the papers in the main are concerned with precision methods of measurement and with instrument design.

Volume 21 comprises some twenty-one papers of very varied character. Selection were invidious but, if mention is to be made of any special papers, those by Dr Dye on a cathode-ray tube method for the harmonic comparison of frequencies, on a magnetometer for the

measurement of the earth's vertical magnetic intensity, on the piezo-electric quartz resonator and its equivalent electrical circuit, and the paper written in collaboration with Dr Hartshorn on a primary standard of mutual inductance, may be noted as exhibiting those qualities of finish and thoroughness which are always to be found associated with Dr Dye's work. Seven of the papers in this volume are concerned with radio problems and include papers on the polarization of radio waves, the cause and elimination of night errors in radio direction-finding, and investigations on wireless waves arriving from the upper atmosphere.

Volume 22 also contains twenty-one papers of which six are directly concerned with wireless problems. Two papers deal with condenser losses and condenser-resistance measurements at radio frequencies and four are concerned with cable problems; the remainder are difficult to classify, but mention may be made of Dr Hartshorn's paper on the measurement of the dielectric constants of liquids, or of Mr Vigoureux's paper on the valve-maintained quartz oscillator.

The two volumes constitute a record of achievement in precision measurements which is altogether encouraging.

A. F.

The Observatories Year Book, 1928 (M.O. 320). Air Ministry Meteorological Office, published by the authority of the Meteorological Committee. Pp. 450. (London: H.M. Stationery Office.) £3. 3s. od.

There is always a satisfaction in perusing a year book of the observatories under the British meteorological service, for it is clearly the work of physicists, not merely of routine observers; we are not left in doubt over the methods of reduction, or over the conditions of exposure at the station, and we have therefore the materials for a satisfactory comparison with corresponding data at other observatories. Thus the distinctions between occasions on which fog, mist and haze are reported are made clear, and we have a table of the objects used in measuring visibility.

The traditional method of estimating base-line values of magnetograph records was to adopt individual readings of the absolute instruments under favourable conditions, and so to trust a comparatively inaccurate instrument liable to change and give no weight to the one that was undisturbed. Now the base-line values adopted are obtained from a curve drawn smoothly through points given by the values deduced from the absolute observations, due allowance being made for discontinuities in the records. This method is far superior in that it tends to eliminate non-systematic errors in the absolute instruments; but unless these measurements are of very reliable pattern some recognition of the magnetographs might perhaps be made by adopting a fraction, say three-fourths, of the change thus obtained.

G. T. W.

Magnetic Phenomena, by SAMUEL ROBINSON WILLIAMS, Ph.D., D.Sc. Pp. xxii + 230. (London: McGraw Hill Publishing Co.) 15s.

The outline of this book differs very considerably from that of the orthodox text-book. "The pages are intended as a guide to the beginner," but the word *beginner* must be interpreted with caution, for, although the treatment is quite elementary, the appeal made is to an inquiring and mature mind. It is not a school book, but a college class book designed to stimulate the spirit of research and inquiry among its readers.

The few pages of mathematics that one meets are of a very simple type, and the book emphasizes in a very healthy manner the importance of physical rather than mathematical thinking. The way in which the author handles his subject is best shown by the titles of his chapters. "Magneto-mechanics," "magneto-acoustics," "magneto-electrics," "magneto-chapters." "Magneto-mechanics," "magneto-acoustics," "magneto-electrics," "magneto-chapters."

"thermics," "magneto-optics," "cosmical magnetism" and "magnetic theories and experimental facts" are the chapter headings of the book taken in order. Throughout, clear accounts are given of the essentials of the experimental methods employed, with a full bibliography of references to original papers.

If a very mild criticism may be hinted, it is that one would like to see fuller reference to English work and English instruments—for example in the chapter dealing with cosmical magnetism, where "current" methods for the measurements of both H and V are hardly sufficiently stressed. The chapter on magnetic theories, although as it stands it is an admirable short summary, could be expanded with considerable advantage. The book fills a niche and may be warmly commended.

A. F.

Physics, Part II, Sound, by W. J. R. CALVERT. Pp. viii + 140. (London: John Murray.)

3s.

Physics, Part III, Light, by W. J. R. CALVERT. Pp. viii + 202. (London: John Murray.) 3s.

An Introduction to Science, by P. E. ANDREWS, B.A., B.Sc., and H. G. LAMBERT, B.Sc., A.I.C. (London: Longmans, Green and Co., Ltd.) 2s. 6d.

There are signs of the approach of certain long-overdue reforms in the teaching of elementary physics. With the growth of the examination system, when candidates for school examinations are to be reckoned by thousands and by tens of thousands, the tendency to sacrifice teaching to examination necessities becomes yearly more pronounced. Questions are asked which are designed not so much to test the candidates' knowledge and to bring out their power of original thought as to provide material for answers which may be marked at a rate high enough to ensure that the results may be made public within a few weeks of the examination. And text-books follow suit in their treatment of their subjects.

It is tragic, but almost inevitable. Almost, we say, for authors are to be found bold enough to pursue the better path, and publishers with enterprise sufficient to make their work public.

The volumes before us are excellent examples of their kind. Mr Calvert's books on *Sound* and *Light* provide sufficient weapons for the attack on the numerical and algebraical exercises beloved of the average examiner to ensure that the candidate for a school certificate examination will do himself justice. At the same time the treatment is thoroughly lively, is in touch with reality, and is designed to encourage physical thinking rather than wooden juggling with mathematical symbols.

Messrs Andrews' and Lambert's book is more elementary in character, providing a year's course in science for the beginner. The text covers a first course in heat, light, sound, magnetism and electricity, the teaching being conducted for the most part by well-planned and simple experiments designed to make the learner think.

All three volumes can be unreservedly commended.

A. F.

Proceedings of the Institution of Mechanical Engineers. Vol. 1, January May, 1930. Pp. viii + 851. (London: Institute of Mechanical Engineers.)

This volume contains the third Thomas Lowe Gray lecture given by Engineer Vice-Admiral Skelton on "Progress in Marine Engineering," and reports of four other addresses. Of these Mr William Taylor's lecture on "Science and Works Management" calls for special attention, a plea being here put forward for the inclusion of this as a subject in the curriculum of an engineer's training.

The reports of three of the Institution's research committees are given in this volume: (1) The first report of the Welding Research Committee. This work has for its object the study of modern methods of welding metals, and deals chiefly with the application of welded joints to pressure vessels. (2) The sixth and final report of the Steam Nozzles Research Committee. (3) The fourth report of the Wire Ropes Research Committee.

Professor Coker has made a further contribution to his work on photoelasticity in a paper on stresses in cams, rollers, and wheels. An account is given by Messrs Barklie and Davies of their investigations into the effects of surface conditions on the fatigue resistance of metals. It is to be noted here that the practice of the electro-deposition of nickel on steel for the purposes of building up worn parts of machinery and of providing wear-resisting surfaces has become fairly common, but if care is not taken under certain conditions an electro-deposit may lead to a weakening of the machine part.

Considerable space is given to steam generation, and there is in this connexion much valuable information on the use of pulverized fuel. The results of tests carried out on the first "Wood" steam generator are interesting. This boiler is the first radiant-heat boiler to be constructed in this country for the exclusive combustion of pulverized fuel, and its design embodies the important feature of surrounding the combustion chamber with a wall of vertical water-tubes. The results of tests show a remarkable performance from the standpoint of evaporation. The boiler, on account of its lightness and its flexibility, should have an important application not only to steam generation in power stations but on board ship.

A valuable contribution to the technique of testing large steam power units is made by Mr H. L. Gray, who has given an account of some carefully conducted trials made by him at Barton Power Station; in this it is to be noted that there is no economy gained by the use of pulverized fuel unless cheaper coal is available.

There is also an interesting paper on the design, construction, and results of a boiler operating under a pressure of 600 lbs./in.².

In the memoirs of this volume we regret to note the death at the untimely age of 47 of Dr Paul Telford Petrie of Manchester, who acted as reporter of the Steam Nozzles Research Committee.

G. A. W.

Photo-Chemistry, by D. W. G. STYLE, Ph.D. Pp. vii + 96. (London: Methuen and Co., Ltd.) 2s. 6d.

This is the latest publication in the very useful series of monographs on physics edited by Dr Worsnop. No attempt is made within the limits of this half-crown volume to present an account of the mass of chemical data that has been accumulated on this subject, but the author has been most successful in giving an outline of the main achievements and theories, especially from the physical standpoint. It bears throughout the impress of a writer who is himself an enthusiastic worker in this field and Professor Allmand fittingly contributes a preface. The book should prove valuable to students of physics and chemistry; it provides an excellent introduction for those intending to carry out research work in this field.

D. C. J.

The Plant in Relation to Water, by N. A. MAXIMOV; authorized English translation edited, with notes, by R. H. YAPP. Pp. 451. (London: George Allen and Unwin.) 21s. net.

This volume, which is essentially a study of the physiological bases of drought resistance, is the most comprehensive and critical work on the subject in the English language. An immense mass of literature exists which is grouped around this topic, and physiologists are much indebted to Professor Maximov for the pains at which he has been to present a clear and ordered summary thereof.

The book is concerned primarily, as we have said, with a physiological topic, but there is in this particular branch of botany so much that is of interest to the physicist, so much in which the assistance of the physicist is to be desired, that no apology is necessary for introducing the work to the notice of students of physical science.

Naturally in such a subject the mechanism of the transport of water by the plant is a matter of primary importance; and the physical theories that have, from time to time, been devised to explain the laws of this transmission urgently demand the criticism of students trained in the facts and theories of physical science and not likely to make dynamical mistakes in discussing the phenomena: for these, vital though they may be, must be explained in terms of theories which, at least, do not outrage dynamical laws.

Moreover, the instruments employed and the methods of measurement are of compelling interest to physicists, especially to those versed in instrument design. For example, despite the care and skill that have been expended on such a problem as the measurement of relative transpiration, it is not too much to say that no completely satisfactory method has yet been devised which shall give for this important quantity figures sufficiently safe in themselves from criticism to serve as a basis for purely physiological arguments.

Atmometers by means of which transpiration values may be compared; instruments for the measurement of transpiration; self-recording balances for the determination of the relation between transpiration and absorption; porometers by which stomatal movements may be followed and compared; these are but a selection from a number of instruments which, in spite of the care which has been lavished on their design in the past, will well repay the attention of the physicist who is interested in the problems of vegetable life. And he will find no better nor more reliable guide within moderate compass to the use and interpretation of the instruments already employed than the volume under review.

A bibliography of some six hundred entries adds much to the value of the book, which in its English dress owes a great deal to the labour spent on it by the English editor, the late Professor Yapp. It is a melancholy reflection that Professor Yapp, though the final proofs passed through his hands, did not live to see the appearance of the completed work.

A. F.

Colloid Science applied to Biology. A general discussion held by the Faraday Society, 1930. Pp. 197, including figures, plates, and full bibliographies. Price 12s. 6d.

We start with a definition of life. Professor A. V. Hill in the first paper presented at the conference, the proceedings of which are now under review, writes of life in the physico-chemical sense as a "self-perpetuating and generally periodic complex of events, occurring indeed in a medium of matter, depending on the properties of matter, but as distinct from matter as music is from the air in which it is propagated." The Faraday Society did not meet to discuss life, but the physico-chemical states of that matter on which life, as we know it, depends.

Nearly 100 years have passed since the knowledge won by microscopic observations led biologists to the far-reaching conclusion that the simplest living unit, classically called a cell, is essentially an aqueous mass of proteinaceous slime to which the name protoplasm was later given. For example, a certain microscopic viscous entity, now called amoeba, was found to grow and reproduce and was, therefore, shown to be a living unit. Associated with these major attributes of growth and reproduction are the phenomena of the continual exchanges of matter and energy between the organism and its environment and the apparently purposeful responses of the former. Clearly, if the myriad-celled organisms, like elephants, or the giant sequoias of California, are to be satisfactorily conceived of as physico-

chemical systems, the unit of their structure, the cell, must form the basis of such a conception.

Even if it is granted that some influence that is remote from the matter of the organism is necessary to vitalize amoeba and other living units,—a view by no means universally held—there are still legitimate physico-chemical problems, related to protoplasm, the elucidation of which will be of much profit to the biologist. Explicit in the introductory remarks of Sir F. Gowland Hopkins, P.R.S., who was in the chair on the second day of the conference, is his belief that for an adequate description of the periodic complex of events during the life of any organism it will be necessary to determine the physical states of matter in which these events occur. The P.R.S. insists, however, that there is, in organic chemistry, an independent field of importance equal to that of physical chemistry in relation to specific syntheses on which assimilation, and so, also, the formation of the structural elements of organisms, are dependent. Both he and Sir William Hardy, who was invited by Professor T. M. Lowry (President of the Faraday Society), to take the chair on the first day of the session, believe that many obscure biological phenomena will be classified in the future as our knowledge of molecular orientation at interfaces increases.

The analytical study of protoplasm is as fundamental to biology as that of the atom is to physics. The specialized study called cytology aims at describing the structures that are visible under the microscope, and their behaviour and functions. Protoplasm is micro-heterogeneous. It is differentiated into nucleus, with its chromosomes, nucleolus, nuclear sap, etc., and cytoplasm with its plastids, mitochondria, golgi apparatus and other micro-structures. The meeting was periodically reminded of the possession by protoplasm of a visible structure. But beyond the scope of the cytologist is the ultramicroscopic structure that is revealed by the arts and arguments of chemistry, physics, and physiology. For examples, the presence of very thin membranes, possibly of unimolecular thickness only, with amazing properties, can be argued: and differences of electrical potential between different parts of a given cell may be deduced: and invisible systems possessing specific chemical activity, called enzymes, can be proved to exist in protoplasm.

Chemical analysis has shown that cytological structures are chiefly composed of proteins, either free or physically associated, or possibly even chemically combined, with lipoids or with nucleic acid. Sterols, phosphatides, carbohydrates and other organic substances are now known to be invariably present in small quantities, as are also mineral salts and water. The idea was advanced towards the end of last century that protoplasm consists of a giant molecule with unstable side-chains. There was never any evidence for this view, and it is now considered that it would be just as accurate to say that a structure, such as Westminster Abbey, or a functioning machine, such as a Rolls Royce car, are respectively composed of giant molecules. The micro-architecture of a cell, and also cell activities, are now attributed to a complex physical association of an unique kind, in an aqueous saline medium, of the various organic compounds found by analysis in protoplasm. What is the nature of this structure, and how is the machine-like precision of its work governed? Most biologists and biochemists, but not all, find it helpful to construct pictures of cell structures; in these, membranes and active surfaces are prominent. From time to time the picture are altered; something is added, something erased. That made by Professor R. A. Peters, and framed in the book under review, deserves careful study, as do the remarks of those who were present at the private view of it. How far any such pictures represent the real state of things cannot be determined, however, until much more purely physico-chemical work is done.

Although it was clearly recognized immediately after Thomas Graham's pioneer work, in the middle of last century, that the proteins and other organic compounds exist in protoplasm in the colloidal state, the chemist, as the P.R.S. reminds us, paid no regard to slimes until towards the close of the century; they were only fit for the sink. Thus the science of colloidics, as Professor Wo. Ostwald, who was present at the symposium, calls

it, is still in its infancy. The subject matter of part I of this discussion shows, quite obviously, that the physical work that is proceeding on protein-water-electrolyte* systems may well be forming a background for a truer picture of the structures in and the properties of living matter than any as yet in existence. Comparing, however, the complexity of protoplasm—in which there are many different kinds of proteins, other organic substances, an array of ions, and water (and even water, according to Gortner, may be present in two different states)—with the relative simplicity of protein-water-electrolyte systems, we at once see that the systematic intellectual construction of a whole, in which there are so many variables, by summation of its parts forms a task of such immensity that a life of centuries is assumed for the infant science of colloidics in its relation to biology.

M. T.

* A big advance in recent years (see Prof. Svedberg's contribution to the general discussion after Prof. Pauli's paper) is that well-defined mineral-free proteins can now be separated from vegetable and animal material. The physical constants characterizing these proteins are not changed by re-crystallization.

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